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STRUCTURE AND PROPERTIES OF TUNGSTEN-BASE POWDER METALLURGY COMPOSITES

by Thomas P. Herbell, John W. Weeton, and Max Quatner

*Lewis Research Center
Cleveland, Ohio*





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STRUCTURE AND PROPERTIES OF TUNGSTEN-BASE POWDER METALLURGY COMPOSITES

by Thomas P. Herbell, John W. Weeton, and Max Quatnetz
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SUMMARY

Tungsten and tungsten-base billets were prepared and extruded in order to determine the strengths of composites produced by promising powder metallurgy methods and to relate microstructure and other metallurgical parameters to these strengths. Two different types of tungsten-base composite powders were utilized. One (tungsten - 5 volume percent of either hafnia, zirconia, or thoria; and tungsten - 0.5 weight percent zirconium) was prepared by the reduction of mixed oxides derived from the chemical solution and calcination of metallic salts. The other (tungsten - 0.5 weight percent zirconium) was prepared by the mechanical comminution of an arc-melted ingot. Both of these basic powder types as well as various combinations with tantalum powder were studied. Most of the materials exhibited 3000^o F tensile and stress-rupture strengths that greatly exceeded those of unalloyed tungsten. Stress-rupture tests at 3500^o F also indicated an appreciable strength advantage relative to tungsten. Strengthening occurred despite the fact that a uniform distribution of dispersoids was generally not achieved. Improved high-temperature properties were attributed in most cases to the combined effects of dispersoids and solid solution alloying. Materials showing particular promise were tungsten - 5 volume percent hafnia, and tungsten - 0.5 weight percent zirconium plus 5 to 15 weight percent tantalum. Tungsten - 0.5 weight percent zirconium plus 5 weight percent tantalum was prepared with a two-phase structure. This material possessed good high-temperature strength properties (twice those of unalloyed tungsten) and was easy to extrude. The strengthening was attributed to the presence of a two-phase structure (one tungsten rich, one tantalum rich) combined with a uniform distribution of fine dispersoids. Presumably the presence of the tantalum-rich phase aided in the extrusion of this material.

INTRODUCTION

Tungsten, with a melting point of 6170^o F (3410^o C), has long been considered a promising material for extremely high-temperature applications. Commercially pure tungsten, however, possesses a high ductile-brittle transition temperature as well as strength properties that deteriorate rapidly with temperature. Considerable research effort has been devoted to the development of improved tungsten-base materials, particularly by alloying. A major portion of this effort has been concerned with the influence of various metallic and nonmetallic additions on the ductility of the materials, particularly the ductile-brittle transition temperature. With the exception of these, the bulk of the work has related to the determination of room- and elevated-temperature tensile properties. Existing data indicate that the alloying approach offers considerable promise for improved high-temperature properties (refs. 1 to 4).

Dispersion strengthening is an alternate to alloying for obtaining improved high-temperature properties. This approach has been applied to many metals with varying degrees of success. The dispersion strengthening of tungsten has been the subject of several investigations (e. g. , refs. 5 to 12). Although it is conceivable that no dispersoid may be as stable in tungsten (with respect to homologous temperature) as alumina is in aluminum SAP (sintered aluminum product), the possibility of producing a material with exceedingly high strength merits serious consideration. Finally, a recent study (ref. 10) indicates that dispersion-strengthened tungsten with an inherently finer grain size should possess improved low-temperature ductility as well as high-temperature strength. To date, however, neither very high strengths nor dispersion microstructures comparable with aluminum SAP have been obtained with tungsten or tungsten-base alloys by this approach.

A number of different methods have been employed by investigators to incorporate a variety of dispersoids (oxides, carbides, nitrides, etc.) in metallic matrices,¹ all of which have inherent advantages and disadvantages depending on the matrix and dispersoid compositions, blending techniques, and blending media. Among the most successful methods used to date are mixing of ultrafine metal and oxide powders including colloids, comminution of relatively coarse metal and oxide powders to yield intimate mixtures of ultrafine powders, internal oxidation of suitable binary alloy powders, and selective reduction of mixed oxides.

The first two of the preceding methods involve the handling of materials that are gen-

¹Based on chemical and thermodynamic stability, oxides are generally considered more desirable as dispersoids than carbides and other refractory compounds (refs. 13 to 15).

erally both pyrophoric and toxic and thus require the use of elaborate handling and processing facilities. The fabrication of billets from relatively coarse composite powders prepared by either internal oxidation or by the selective reduction of mixed oxides can be accomplished with conventional powder processing equipment. In addition, with lower melting point matrices such as copper and nickel, these last two techniques have yielded some of the strongest, most creep-resistant materials produced to date (refs. 16 to 18).

Based on the preceding factors, several novel methods for producing tungsten-base composites or dispersion-strengthened materials were felt to warrant study. The objectives of this investigation were to determine the strengths of materials produced by some of these promising powder metallurgy methods and where possible relate microstructure and other metallurgical parameters to these strengths.

Tungsten-base composites or dispersion-strengthened tungsten alloys produced by powder metallurgy methods were studied in this investigation. Two different tungsten-base composite powders were utilized. The first was prepared by reduction of mixed oxides derived from the chemical solution and calcination of metallic salts. The second was prepared by the mechanical comminution of arc-melted material. Both of these basic powder types as well as various combinations with tantalum powder were fabricated into billet form and extruded.

A total of 29 tungsten-plus-additive billets were prepared. Elemental tungsten was also processed in a similar manner to serve as base-line data. Extrusion temperatures ranged from 3600^o to 4400^o F, and extrusion ratios ranged from 8:1 to 16:1. Tensile and stress-rupture tests of the as-extruded materials were conducted at temperatures of 3000^o and 3500^o F in vacuum. Chemical and X-ray analyses, lattice parameter, hardness, grain size, density, and both light and electron micrographic studies of the extruded composites were made.

MATERIALS AND PROCEDURE

The materials, compositions, and processing procedures employed in the fabrication and extrusion of the billets are summarized in tables I to IV.

Raw Materials

The raw materials employed included the following:

- (1) Commercial tungsten powder
- (2) Coprecipitated and reduced tungsten-base composite powders containing either 5 volume percent of hafnia, zirconia, or thoria or 0.5 weight percent of zirconium

TABLE I. - PHYSICAL CHARACTERISTICS OF STARTING POWDERS

Powder	Supplier	Method of preparation	Average particle size, μ	Surface area m^2/g	Lattice parameter, \AA	Billets prepared with this powder
Tungsten	General Electric	Reduction	4.2	0.095	3.168	1
Tungsten - 5 volume percent hafnia	Curtiss Wright	Coprecipitation and selective reduction of mixed oxides	5.5	0.110	3.166	2 to 5
Tungsten - 5 volume percent thoria	Curtiss Wright	↓	3.4	0.390	3.167	6 to 8
Tungsten - 5 volume percent zirconia	Curtiss Wright		7.0	0.210	3.165	9, 10
Tungsten - 0.5 weight percent zirconium	Curtiss Wright		Coprecipitation and reduction of mixed oxides	4.0	0.098	3.167
Tungsten - 0.5 weight percent zirconium	Climax Molybdenum	Arc-melted ingot (subsequently comminuted to powder)	12.0	0.088	3.169	13, 16, 23 to 25
Tantalum	Kennametal	Reduction	14.0	0.110	3.306	14 to 30

TABLE II. - CHEMICAL ANALYSIS OF STARTING POWDERS

[Carbon content determined by combustion with chromatographic technique; nitrogen by Kjeldahl analysis; oxygen by inert gas fusion; all others by semiquantitative spectrographic analysis.]

Element or compound	Powder						
	Tungsten	Tungsten-hafnia	Tungsten-thoria	Tungsten-zirconia	Tungsten-zirconium	Tungsten-zirconium	Tantalum
Concentration, weight percent							
C	0.001	0.005	0.002	0.01	0.005	0.009	0.005
N	NA ^a	NA	NA	NA	NA	NA	.028
O	.12	.05	.05	.42	.087	.078	.14
Mg	.001	.002	.001	.001	.002	ND ^b	ND
Al	ND	.001	.001	.001	.001	ND	ND
Si	.001	.07	.05	.03	.06	.001	<.01
Ca	ND	ND	ND	.005	ND	ND	ND
Ti	↓	.001	.003	.002	.002	↓	<.01
Cr	↓	.03	.03	.04	.03	↓	ND
Mn	↓	<.001	.002	ND	.001	↓	ND
Fe	.001	.05	.05	.05	.07	.002	<.01
Co	ND	.002	.001	.002	.001	.03	ND
Ni	↓	.02	.02	.05	.02	ND	ND
Cu	↓	.0005	.0005	.001	.0005	.001	ND
Zr	↓	.05	ND	ND	.51	.49	<.01
Cb	↓	ND	.01	.01	ND	ND	.03
Mo	↓	.002	.002	.002	.002	.001	.15
Pd	↓	.003	ND	ND	.003	ND	ND
Ag	↓	.0005	.001	.0005	<.0005	↓	ND
Cd	↓	.01	ND	ND	.01	↓	ND
Sn	↓	.002	.001	ND	.001	↓	<.01
Re	↓	ND	ND	.001	ND	↓	ND
Ta	↓	<.01	ND	.01	.01	↓	Bal.
Pb	↓	ND	.003	.02	ND	↓	ND
W	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	ND
HfO ₂	ND	2.82	ND	ND	<.005	ND	ND
ThO ₂	NA	NA	2.72	NA	NA	NA	NA
ZrO ₂	NA	NA	NA	1.71	NA	NA	NA

^aNot analyzed.

^bNot detected.

TABLE III. - ADDITIVE CONCENTRATION IN TUNGSTEN-BASE COMPOSITES

Composite	Additive	Concentration, weight percent			Billet
		Oxide	Zirconium	Tantalum	
Tungsten plus oxides	Hafnia	2.8	----	--	2 to 5
	Thoria	2.7	----	--	6 to 8
	Zirconia	1.7	----	--	9 and 10
Tungsten plus zirconium	Zirconium	---	0.5	--	11 to 13
Tungsten plus zirconium and tantalum	Zirconium and tantalum	---	0.48	5	14 to 16
		---	.45	10	17 and 18
		---	.43	15	19 and 20
		---	.40	20	21 to 25
Tungsten plus oxides and tantalum	Hafnia and tantalum	2.26	----	20	26 and 27
	Thoria and tantalum	2.18	----	20	28
	Zirconia and tantalum	1.37	----	20	29 and 30

(3) Arc-melted and comminuted tungsten - 0.5 weight percent zirconium

(4) Capacitor-grade tantalum powder

The measured physical properties and chemical analyses of these materials are presented in tables I and II.

Of the 30 billets prepared, one was elemental tungsten; the remaining billets were of the nominal chemical analysis shown in table III. For convenience, the description of the various materials produced is divided into the following categories: tungsten, tungsten plus oxides, tungsten plus zirconium, tungsten plus zirconium and tantalum, and tungsten plus oxides and tantalum.

Tungsten

Commercially pure tungsten powder was processed into billets by procedures that will be described in the section entitled Consolidation. The properties of such a material processed in a manner similar to that utilized for the composite materials were felt to be a reasonable standard for comparison.

Tungsten Plus Oxides

At the time this research program was initiated it was learned that the Curtiss Wright

Corporation had developed a versatile process for the production of alloy, cermet, carbide, and ceramic powders (Triffelman process, ref. 19). The process involves the dissolution of metallic elements in a suitable solvent followed by flash drying, calcination, and finally reduction of the resulting mixed oxides. It was believed that the process could be used to produce powders for an oxide-dispersion-strengthened product. For example, by the selective reduction of mixed oxides a relatively unstable matrix oxide could be reduced to the metallic state while maintaining a uniform dispersion of a high-stability oxide.

Preliminary studies indicated that while a high-stability oxide could be produced in a metallic powder matrix, many of the oxide particles were larger than desirable for dispersion-strengthened products. However, whether the observed large oxides were present in the initial powder or whether they were the result of processing and consolidation treatments was not known. Furthermore it was believed that there might also be fine oxide dispersoids distributed among the large ones. Thus materials of this type had to be processed into a consolidated or extruded form to permit a more thorough examination by electron microscopy techniques and to evaluate their mechanical properties. In view of the fact that the oxides observed in these materials were relatively large, they were classified as tungsten-plus-oxide composites rather than dispersion-strengthened materials.

Tungsten Plus Zirconium

Tungsten-plus-zirconium alloy powders were prepared by two different methods. The first was prepared by the Triffelman Process described in the preceding section, and the second by an arc-melting process. For the arc-melted material, an ingot was cast and machined to chips. Subsequently the machined chips were comminuted into powders by a ball milling process. In both instances the majority of the zirconium that was added to the tungsten matrix was in solid solution. During consolidation and fabrication it was felt that enough oxygen would be picked up by the zirconium to convert it into zirconium oxide, which would strengthen the tungsten. In other words, the material was to be internally oxidized by the processing treatments.

Tungsten Plus Zirconium and Tantalum

The two types of tungsten-plus-zirconium powder just described were also combined with various amounts of capacitor-grade tantalum powder. It was felt that the zirconium would act as a scavenger of interstitial impurities to form dispersoids and that the tanta-

lum would act as a ductile phase, an oxygen source, and a solid-solution alloying element.

Tungsten Plus Oxides and Tantalum

Composites were produced by combining the three types of tungsten-plus-oxide powders with various amounts of tantalum powder. It was envisioned that the tantalum would act as a ductile phase during the extrusion process as well as to offer the possibility to alloy and strengthen the matrix. The tungsten-plus-oxide powders were those produced by the Triffleman Process and the tantalum was capacitor grade.

Cleaning

In order to minimize undersirable impurity oxides, some of the billets were prepared from powders that had been precleaned in flowing hydrogen prior to compaction. (For the tantalum-bearing alloys, only the tungsten-base portion of the composite was cleaned.) Cleaning was accomplished by passing purified hydrogen through a vertical packed column of the powder at a rate of 5 to 15 cubic feet per hour. The temperature of the powder bed was raised slowly to 1500^o to 1600^o F and then held at this temperature until the moisture level of the effluent hydrogen was equal to that of the affluent hydrogen, approximately 10 parts per million. The total time at temperature was generally about 8 hours. The rate of temperature rise in the powder was dictated by the restriction that the moisture level of the effluent hydrogen should not exceed 1000 parts per million as measured by a phosphorus pentoxide electrochemical moisture meter. This restriction was intended to prevent localized overheating and possible sintering of the powder.

Consolidation

Powder consolidation was effected by one of two procedures. Billets prepared from the elemental tungsten or the coprecipitated tungsten composite or alloy powders were hydrostatically compacted at room temperature followed by a combination of hydrogen and vacuum sintering. Billets prepared from the arc-melted and comminuted tungsten alloy were hot pressed in double-acting graphite dies followed in most cases by vacuum sintering. (In order to minimize possible carbon contamination, approximately 7/16 inch was removed from the surface of the hot-pressed billets prior to vacuum sintering.)

Cold pressing. - Reusable rubber pressing "boots" backed up by perforated steel retaining cans were loaded with powder, handtamped to ensure proper fill, sealed with a

clamp, and hydrostatically compacted at either 30 000 or 50 000 psi. Proper sizing of the pressing "boots" ensured a minimum of machining for canning and extruding in nominally 2-inch extrusion hardware.

Sintering. - Sintering of the cold-compacted billets was accomplished in a resistance-heated tungsten-element furnace. Those containing tantalum were treated 4 to 6 hours at 4000^o F in a vacuum of approximately 5×10^{-5} torr. Billets without the tantalum addition were given a duplex sintering treatment consisting of a hydrogen presinter followed by 4 hours in vacuum at 4000^o F. The initial billets prepared in this manner received an 8-hour presinter at 2850^o F in hydrogen. In order to reduce grain growth and oxide agglomeration, which was observed in the earlier sintering process, a new schedule was devised; namely, the hydrogen presintering was reduced to 2 hours at 2600^o F. This schedule resulted from the microstructural examination of a series of small tungsten - 5 volume percent thoria pellets compacted at 30 000 psi and sintered for various times and temperatures in both hydrogen and vacuum.

Hot pressing. - Billets prepared from powders derived from arc-melted tungsten plus zirconium were not successfully compacted at hydrostatic pressures up to 100 000 psi. These billets were therefore hot-pressed in double-acting graphite dies. One billet in this series (billet 16) was pressed at 4000 pounds per square inch for 1 hour at 2700^o F in a vacuum of approximately 1×10^{-3} torr. This billet received no subsequent vacuum sintering. The remaining five billets were pressed at 1000 pounds per square inch for 1/2 hour at 3300^o F in a high-purity argon atmosphere (99.998 percent argon). These billets were subsequently sintered for 4 hours at 4000^o F in a vacuum of 5×10^{-5} torr.

Canning

Of the 30 billets prepared for extrusion, 27 were canned in 1/4-inch-thick pressed and sintered molybdenum cans. The shape and dimensions of the extrusion billets and cans are shown in figure 1. In order to insure cleanliness, all machining operations both with respect to the billets and to the cans were done without lubrication. As a final precaution, once a given billet and its accompanying can were machined, the two were fitted together, a lid was inserted, and the entire assembly was heated at 4000^o F for 2 hours in a vacuum of 5×10^{-5} torr. (This 2-hour treatment in vacuum had the effect of an additional sinter and is indicated as such in table IV (p. 12).) The cleaned billet assemblies were then sealed by electron-beam welding to insure minimum contamination during handling and heating prior to extrusion.

The three remaining billets (billets 15, 18, and 20) exhibited extensive surface cracks. These billets were canned in tungsten in an attempt to salvage them. This canning was accomplished by placement of the unmachined billets (completely surrounded by

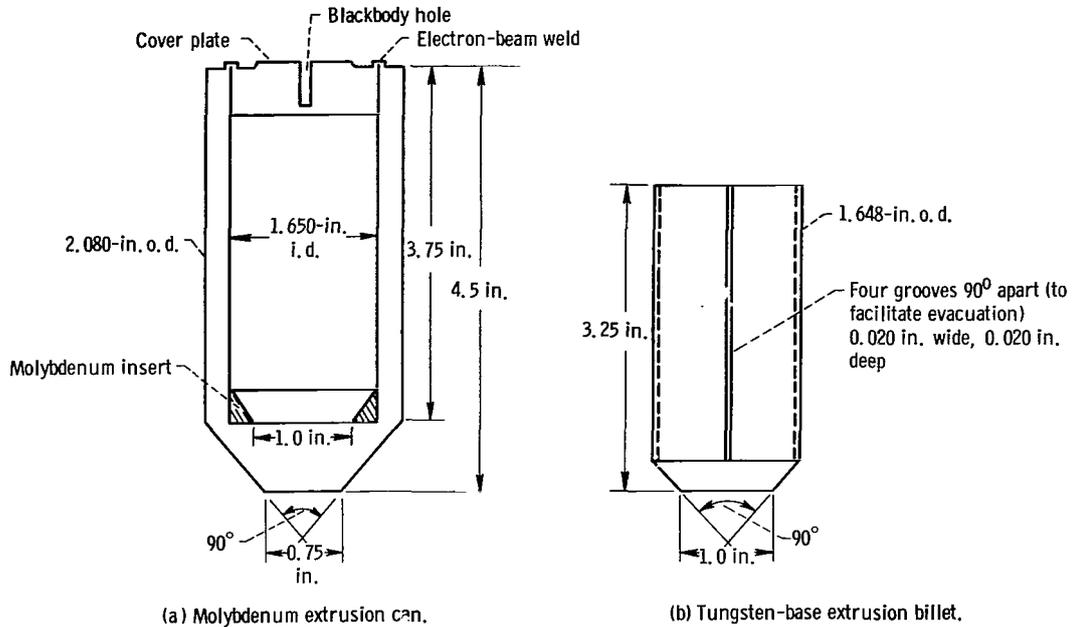


Figure 1. - Extrusion billet and can.

1-micron tungsten powder) in rubber pressing boots and hydrostatically compacting the composites at 50 000 pounds per square inch. After they were sintered for 2 hours at 4000° F in vacuum, the billets were machined to the same dimensions as were the molybdenum-canned billets.

Extrusion

A vertical three stage 1020 ton Loewy hydropress (described in ref. 20) equipped with nominal 2-inch-diameter tooling (maximum stem pressure 200 000 psi) was used for the extrusion operations. Billets were inductively preheated in flowing hydrogen to temperatures of 3600° to 4400° F, transferred to the press (transfer time 4 to 7 sec), and extruded through zirconium-oxide-coated 90° tool steel dies. All billets were extruded at a nominal reduction ratio of 12:1 except billet 4 (16:1), billet 22 (8:1), and billet 23 (6:1). Under these conditions, maximum measured extrusion pressures were from 115 000 to 199 600 psi with ram speeds of from 2.2 to 12.8 inches per second.

Examination and Evaluation

Extruded bars were examined both visually and radiographically for flaws, cut into test pieces for metallographic examination and for the determination of density, chemical

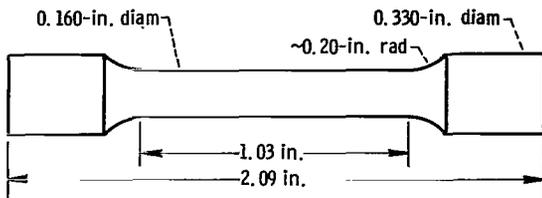


Figure 2. - Tensile and stress-rupture specimen.

analysis, lattice parameter, room-temperature hardness, grain size, and elevated-temperature tensile and stress-rupture properties.

Tensile and stress-rupture testing. - Specimens for both tensile and stress-rupture testing were machined from the as-extruded billets.

The specimens had a reduced section 1.03 inches in length and 0.160 inch in diameter, as shown in figure 2.

Tensile tests at 3000^o and 3500^o F were conducted on a screw-driven Instron tensile machine equipped with a water-cooled vacuum chamber (1×10^{-5} torr) and a tantalum sleeve heater. Crosshead speed was 0.02 inch per minute. A strip-chart recording of load as a function of displacement was made for each test. Reduction in area at the fracture edge of the specimens was also determined.

Constant-load stress-rupture tests were conducted in a conventional beam-loaded machine equipped with a water-cooled vacuum shell (5×10^{-5} torr) and a tantalum heater. The majority of these tests were conducted by a commercial laboratory. Sample extensions were measured from loading rod movement.

Density. - Density was determined by mercury displacement (accuracy ± 0.02 g/cu cm). The reported values are the average of two tests.

Hardness. - Microhardness was determined with a 136^o diamond-pyramid indenter using a 200-gram load. Five readings were averaged for each determination.

Lattice parameter. - Lattice parameter measurements were obtained with an X-ray diffractometer utilizing Cu-K α radiation and a nickel filter. The accuracy of the determinations was ± 0.0002 angstrom. The measurements were made to determine the extent of solutioning resulting from the consolidation processes.

Grain size. - Grain size was determined by counting the number of grains intercepted by a 48.3-centimeter circle at a magnification of 640 and by using the formula

$$D = C/MN$$

where

- D average grain diameter, cm
- C circumference of circle, cm
- M magnification
- N number of intercepts

Three counts were averaged for each determination.

TABLE IV. - TUNGSTEN BILLET COMPOSITION AND PROCESSING

Billet	Nominal additive composition (a)	Consolidation				Extrusion ^{b, c}				Remarks
		Hydrostatic compacting pressure, psi	Hydrogen presintering		Vacuum sintering time at 4000° F, d hr	Temperature, °F	Transfer time, sec	Maximum extrusion pressure, psi	Ram speed, in./sec	
			Time, hr	Temperature, °F						
e ₁	None	30×10 ³	8	2850	4	3800	7	123.7×10 ³	3.2	
2	5 Hafnia	↓	8	2850	↓	4000	4	141.7	3.8	
e ₃	5 Hafnia		2	2600		4000	5	116.3	4.2	
e ₄	5 Hafnia		2	2600		4000	5	152.7	3.0	
e ₅	5 Hafnia		2	2600		3600	5	155.7	3.8	
e ₆	5 Thoria	30×10 ³	8	2850	4	3800	7	-----	---	Sticker, no specimens
e ₇	5 Thoria	30	2	2600	4	4200	5	173.6×10 ³	6.0	
e ₈	5 Thoria	30	2	2600	4	4300	6	161.7	7.0	
9	5 Zirconia	30×10 ³	8	2850	6	4000	7	160.9×10 ³	3.0	
e ₁₀	5 Zirconia	30	2	2600	6	4000	--	151.6	2.2	
11	0.5 Zirconium	30×10 ³	8	2850	4	4000	6	137.7×10 ³	6.0	
e ₁₂	0.5 Zirconium	30	2	2600	4	4000	5	120.2	4.8	
13	0.5 Zirconium	Hot pressed ^f	--	----	6	4200	6	197.0	6.6	
14	0.47 Zirconium and 5 tantalum	50×10 ³	--	----	6	4200	7	148.6×10 ³	7.2	
15	0.47 Zirconium and 5 tantalum	50	--	----	6	4400	5	181.5	5.2	
16	0.47 Zirconium and 5 tantalum	Hot pressed ^g	--	----	--	4000	5	115.0	8.0	
17	0.45 Zirconium and 10 tantalum	50×10 ³	--	----	6	4400	6	167.6×10 ³	11.6	
18	0.45 Zirconium and 10 tantalum	50	--	----	6	4400	--	179.6	3.4	
19	0.42 Zirconium and 15 tantalum	50×10 ³	--	----	6	4400	6	189.6×10 ³	2.6	
20	0.42 Zirconium and 15 tantalum	50	--	----	6	4400	--	199.6	2.6	
21	0.40 Zirconium and 20 tantalum	50×10 ³	--	----	6	4000	7	-----	----	Sticker, no specimens
22	0.40 Zirconium and 20 tantalum	50	--	----	↓	4400	5	137.7×10 ³	8.0	
23	0.40 Zirconium and 20 tantalum	Hot pressed ^f	--	----	↓	4200	4	115.8	12.8	No specimens
24	0.40 Zirconium and 20 tantalum	Hot pressed ^f	--	----	↓	4200	5	-----	----	Sticker, no specimens
25	0.40 Zirconium and 20 tantalum	Hot pressed ^f	--	----	↓	4200	7	-----	----	Sticker, no specimens
26	4 Hafnia and 20 tantalum	30×10 ³	--	----	6	4300	6	190.0×10 ³	4.0	
27	4 Hafnia and 20 tantalum	30	--	----	6	4300	6	147.7	6.0	
28	4 Thoria and 20 tantalum	30×10 ³	--	----	6	4200	6	-----	---	Sticker, no specimens
29	4 Zirconia and 20 tantalum	30×10 ³	--	----	6	4000	--	162.5×10 ³	3.6	No specimens
30	4 Zirconia and 20 tantalum	30	--	----	6	4000	--	186.6	3.0	No specimens

^aAll oxides given in volume percent; all other additives given in weight percent.

^bAll billets canned in 1/4-in. -thick powder-metallurgy molybdenum except billets 15, 18, and 20, which were canned in powder-metallurgy tungsten.

^cReduction ratio, 12:1 except billet 4(16:1), billet 22(8:1), and billet 23(6:1).

^dIncludes 2 hr required to clean billet-can assembly prior to welding.

^eTungsten-base powder hydrogen precleaned for 8 hr at 1550° F prior to compacting.

^fHot pressed at 1000 psi for 1/2 hr at 3300° F (argon atmosphere).

^gHot pressed at 4000 psi for 1 hr at 2700° F (vacuum).

RESULTS

Table IV contains a summary of the consolidation and extrusion operations utilized. Test specimens were obtained from a total of 21 billets. Seven of the nine billets that either did not extrude or yielded no material suitable for testing were those that contained 20 weight percent of tantalum. In addition several billets with tantalum were severely cracked during extrusion: billets 26 and 27 (5-volume percent hafnia plus 20 weight percent tantalum) and billet 18 (0.45 weight percent zirconium plus 10 weight percent tantalum). All of the remaining billets appeared both visually and radiographically sound.

Tensile and Stress-Rupture Properties

Results of the stress-rupture tests carried out on the as-extruded tungsten and tungsten-base composites are given in table V. Stress-rupture strengths are plotted in figures 3 to 7. In addition, these figures also contain tensile strength values, which were considered to be equivalent to 0.1-hour stress-rupture tests. Figure 8 contains a bar graph summary of both tensile strengths and the stresses required for failure in 10 and 100 hours at a test temperature of 3000^o F.

Because of machining difficulties, only a limited number of test specimens were available for many of the composite materials. A screening test based on the life at a stress of 8000 psi was employed for the purpose of comparing the strength properties of the various materials tested. This data is given in figure 9 for both 3000^o and 3500^o F tests.

Tungsten. - Stress-rupture data for unalloyed tungsten are shown in figure 3. At 3000^o F, the estimated stresses for 10- and 100-hour life were 7200 and 5000 psi, respectively. At a stress of 8000 psi the observed life was 8.8 hours at 3000^o F and 0.16 hour at 3500^o F. These values compare favorably with other powder-metallurgy tungsten produced previously at this laboratory (ref. 21).

Tungsten plus oxides. - Three tungsten-plus-oxide composite powders were evaluated (tungsten-hafnia, tungsten-zirconia, tungsten-thoria). For convenience, the results of tests carried out on extruded specimens of these materials will be described separately in the following sections.

Tungsten plus hafnia: Figure 4 shows the 3000^o and 3500^o F stress-rupture strengths of the tungsten-hafnia composites extruded at 12:1 and 16:1 both with and without a hydrogen precleaning treatment. At 3000^o F the material that exhibited the best strength

TABLE V. - EXPERIMENTAL RESULTS

Billet	Nominal matrix additive	Stress-rupture properties					General properties (as-extruded specimens)						
		Temperature, °F	Stress, psi	Life, hr	Reduction in area, percent	Elonga- tion, percent	Measured density, g/cu cm	Percent of theoretical density (a)	Lattice param- eter, Å	Diamond pyramid hardness (200-g load)		Average grain diameter, cm	
										Longi- tudinal	Trans- verse	Longi- tudinal	Trans- verse
1	None	3000	14 000	b _{0.1}	44.5	36.4	19.24	99.4	3.167	372	371	0.0025	0.0022
		↓	10 000	1.8	26.2	----							
			9 000	3.8	23.5	----							
			8 000	8.8	70.9	57.0							
			6 000	18.6	63.6	52.0							
			3500	8 000	(c)	(d)							
2	5 volume percent hafnia	3000	21 500	b _{0.1}	47.4	58.8	18.98	100.6 (100.0)	3.164	402	413	0.0044	0.0038
		3000	15 000	16.1	----	27.0							
		3000	13 000	9.6	69.4	47.0							
3	5 volume percent hafnia	3000	20 500	b _{0.1}	44.4	56.0	19.07	101.1 (100.1)	3.166	373	415	0.0030	0.0019
		3000	15 000	8.7	53.9	48.0							
		3000	12 000	73.8	38.0	47.0							
4	5 volume percent hafnia	3000	30 100	b _{0.1}	34.3	36.0	19.03	101.1 (99.8)	3.164	398	426	0.0022	0.0016
		3000	20 000	3.5	54.4	56.0							
		3000	13 000	77.8	----	27.0							
		3500	23 900	b _{0.1}	7.5	12.6							
		↓	8 000	4.3	17.5	----							
			6 000	3.1	42.2	----							
5	5 volume percent hafnia	3000	22 700	b _{0.1}	24.8	34.2	19.00	100.8 (100.5)	3.167	419	429	0.0011	0.0008
		3000	15 000	4.2	18.3	18.0							
		3000	12 000	81.6	(d)	32.0							
7	5 volume percent thoria	3000	8 000	27 (min)	2.5	----	18.66	98.8 (98.0)	3.166	395	394	0.0014	0.0014
		3000	8 000	9 (min)	3.5	----							
		3000	7 000	8 (min)	2.5	----							
8	5 volume percent thoria	3000	8 000	44 (min)	3.0	----	18.70	99.1 (98.1)	3.162	---	---	-----	-----
		↓	8 000	6 (min)	2.7	----							
			8 000	5 (min)	2.5	----							
			7 000	11 (min)	2.5	----							
9	5 volume percent zirconia	3000	39 300	b _{0.1}	3.4	10.8	18.77	99.4 (98.7)	3.163	379	371	0.0030	0.0027
		3000	17 000	3.8	(d)	6.0							
		3000	7 000	26.8	(d)	19.0							
		3500	8 000	1.9	16.9	----							
		3500	6 000	e, 3	1.0	----							
		3500	4 000	17.4	19.7	----							

^aBased on nominal starting chemistry; values in parenthesis based on chemical analysis of extruded specimens.

^bTensile test.

^cBroke on loading.

^dRadius failure.

^eCracked specimen.

TABLE V. - Continued. EXPERIMENTAL RESULTS

Billet	Nominal matrix additive	Stress-rupture properties					General properties (as-extruded specimens)							
		Temperature, °F	Stress, psi	Life, hr	Reduction in area, percent	Elonga- tion, percent	Measured density, g/cu cm	Percent of theoretical density	Lattice param- eter, Å	Diamond pyramid hardness (200-g load)		Average grain diameter, cm		
										Longi- tudinal	Trans- verse	Longi- tudinal	Trans- verse	
10	5 Volume percent zirconia	3000	19 300	^b 0.1	17.2	30.2	18.65	100.0 (98.1)	3.165	378	369	0.0018	0.0016	
		↓	20 000	.1	17.0	29.5								
			12 000	4.7	(d)	8.0								
			7 000	48.6	5.3	24.0								
			3500	8 000	.5	18.5								----
11	0.5 Weight percent zirconium	3000	17 600	^b 0.1	100	66.0	19.02	99.4 (100.2)	3.163	359	375	0.0032	0.0026	
		↓	12 000	4.7	63.0	----								
			11 000	6.2	46.3	----								
			10 000	9.7	49.1	----								
			8 000	38.5	36.9	----								
12	0.5 Weight percent zirconium	3000	16 400	^b 0.1	16.9	22.0	18.98	99.2 (99.2)	3.164	381	388	0.0022	0.0017	
		↓	10 000	.6	8.62	----								
			8 000	4.4	43.8	----								
			6 000	4.0	10.6	----								
13	0.5 Weight percent zirconium	3000	8 000	283	4.3	----	18.84	98.3 (98.5)	3.170	451	454	0.0005	0.0004	
		↓	3500	8 000	5.5	7.8								----
14	0.47 Weight percent zirconium + 5 weight percent tantalum	3000	36 500	^b 0.1	2.9	11.6	18.82	98.9 (101.5)	3.179	388	402	0.0013	0.0011	
		↓	3000	21 000	4.6	1.0								5.0
			3000	14 000	50.1	(d)								6.0
			3500	20 600	^b .1	6.5								12.6
				8 000	1.8	3.5								----
				6 000	4.4	3.4								----
		4 000	20.8	4.9	----									
15	0.47 Weight percent zirconium + 5 weight percent tantalum	3000	33 500	^b 0.1	0	7.4	18.72	98.6 (101.9)	3.172	463	478	0.0007	0.0007	
		↓	3000	20 000	7.0	----								7.0
			3000	14 000	^e 2.2	^d 1.0								4.0
			3500	19 500	^b .1	6.3								19.0
16	0.47 Weight percent zirconium + 5 weight percent tantalum	3000	8 000	379	(d)	9.9	18.60	98.0 (97.4)	3.174	466	---	0.0006	-----	
		↓	3000	7 000	^f 881	----								6.0
17	0.45 Weight percent zirconium + 10 weight percent tantalum	3000	22 400	^{b, e} 0.1	34.2	44.0	18.71	99.2 (101.9)	3.183	426	409	0.0015	0.0012	
		↓	3000	17 000	3.8	----								48.0
			3000	10 000	^f 26.0	4.4								4.0
			3500	22 300	^{b, f} 1.1	5.9								7.6
				8 000	^f 1.6	2.4								----

^aBased on nominal starting chemistry; values in parenthesis based on chemical analysis of extruded specimens.^bTensile test.^cBroke on loading.^dRadius failure.^eCracked specimen.^fTest incomplete, furnace failure.

TABLE V. - Concluded. EXPERIMENTAL DATA

Billet	Nominal matrix additive	Stress-rupture properties					General properties (as-extruded specimens)						
		Temperature, °F	Stress, psi	Life, hr	Reduction in area, percent	Elonga- tion, percent	Measured density, g/cu cm	Percent of theoretical density (a)	Lattice param- eter, Å	Diamond pyramid hardness (200-g load)		Average grain diameter, cm	
										Longi- tudinal	Trans- verse	Longi- tudinal	Trans- verse
18	0.45 Weight percent zirconium + 10 weight percent tantalum	3000	38 800	^b 0.1	2.9	8.4	18.70	98.4 (101.8)	3.177	405	397	0.0016	0.0013
		3000	24 000	7.2	---	6.0							
		3000	14 000	67.8	---	15.0							
		3500	24 500	^b .1	---	14.8							
		3500	8 000	3.8	3.8	----							
19	0.42 Weight percent zirconium + 15 weight percent tantalum	3000	40 400	^b 0.1	3.4	11.2	18.68	99.7 (103.5)	3.184	446	497	0.0009	0.0006
		3000	25 000	3.6	---	3.4							
		3000	15 000	67.7	(d)	42.0							
20	0.42 Weight percent zirconium + 15 weight percent tantalum	3000	44 000	^b 0.1	4.3	12.8	18.67	98.83 (99.5 to 103.3)	3.179	416	419	0.0030	0.0014
		3000	15 000	59.2	(d)	17.0							
		3500	8 000	1.1	3.0	----							
26	4 Volume percent hafnia + 20 weight percent tantalum	3000	22 700	^b 0.1	23.6	32.4	18.98	103.7	3.188	434	455	0.0007	0.0006
		3000	8 000	3.5	8.8	----							
		3500	8 000	1.5	6.7	----							
		3500	6 000	.4	2.4	----							
27	4 Volume percent hafnia + 20 weight percent tantalum	3500	4 000	57.8	17.7	----	18.55	101.4 (104.3)	3.188	477	478	0.0008	0.0007

^aBased on nominal starting chemistry; values in parenthesis based on chemical analysis of extruded specimens.

^bTensile test.

^cBroke on loading.

^dRadius failure.

^eCracked specimen.

^fTest incomplete, furnace failure.

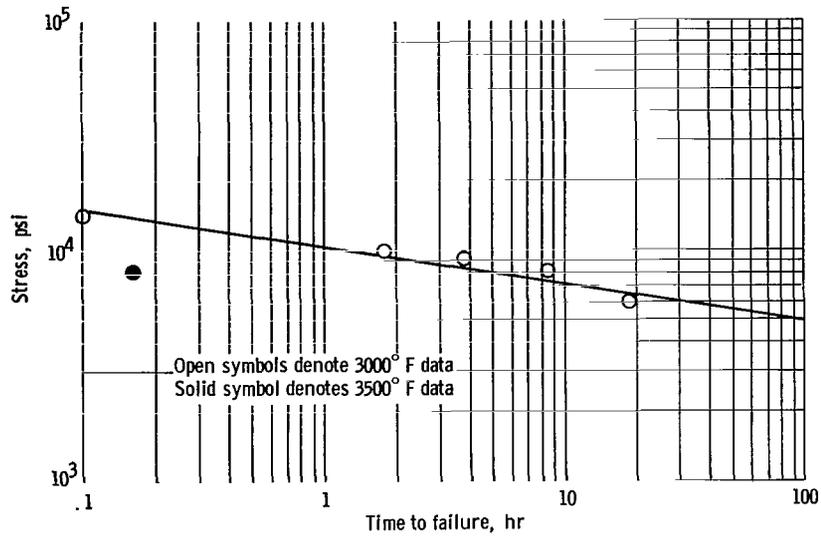


Figure 3. - Stress-rupture strength of unalloyed tungsten (billet 1). Reduction ratio, 12:1. Extrusion temperature, 3800° F.

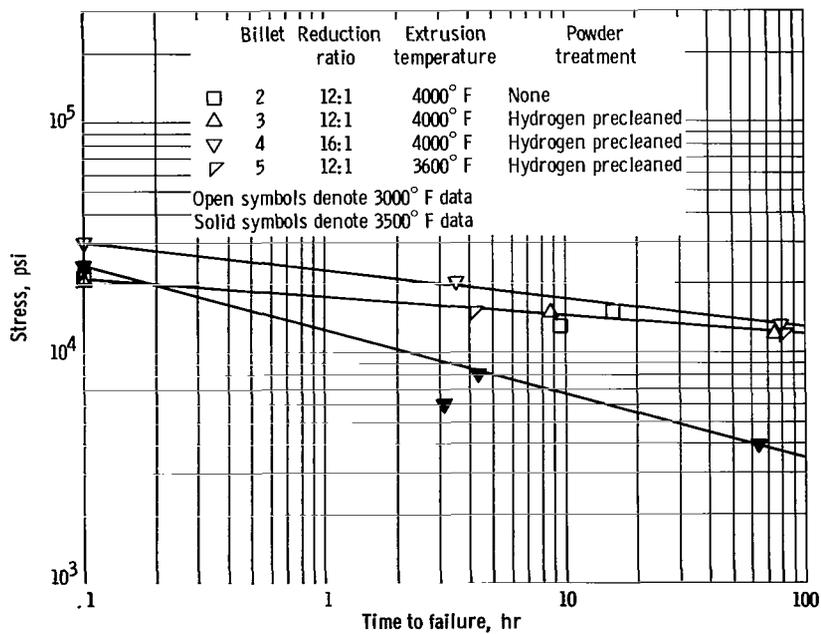


Figure 4. - Stress-rupture strength of tungsten - 5 volume percent hafnia composites.

properties was prepared from hydrogen-precleaned powder and extruded at a ratio of 16:1 at 4000^o F. Materials processed differently were somewhat lower in strength. When a life of 100 hours was reached, the estimated 3000^o F strengths of all the hafnia materials were approximately the same.

For the time interval studied (which ranged from 0.1 to 100 hr) the strengths were in all cases considerably superior to those of unalloyed tungsten. For example, at a life of 100 hours the tungsten-hafnia composites exhibited 3000^o F rupture stresses of up to 13 000 psi relative to an extrapolated value of about 5000 psi for unalloyed tungsten. An alternate approach to the comparison of stress-rupture properties is to consider the time required to cause failure under the conditions of constant load. At a stress of 8000 psi, the best of the tungsten-hafnia materials exhibited an extrapolated life at 3000^o F of 10 000 hours (fig. 9). This represents an improvement in stress-rupture life over unalloyed tungsten of more than three orders of magnitude.

The tungsten-hafnia material extruded at 16:1 and 4000^o F was also tested at 3500^o F. As can be seen in figure 4, the rupture strength decreased more rapidly with increasing time than for the 3000^o F tests. Despite this rapid decrease, its tensile, or 0.1-hour stress-rupture strength (23 900 psi), was only slightly below that of the 3000^o F test. Furthermore, under these test conditions this material was stronger at 3500^o F than the remaining tungsten-hafnia materials were at 3000^o F.

The stress-rupture results shown in table V also indicate that the tungsten-hafnia composites exhibited an appreciable amount of ductility. In general, both the fracture elongation and reduction in area measurements obtained were of about the same order of magnitude as those for unalloyed tungsten. There appeared, however, to be no correlation between the ductility values and the observed strength levels.

Tungsten plus zirconia: Stress-rupture strengths of the tungsten-zirconia composites extruded at 12:1 and 4000^o F both with and without hydrogen precleaning are shown in figure 5. At 3000^o F, the material that did not receive a hydrogen precleaning treatment prior to consolidation exhibited short time strength properties that were somewhat superior to those of the precleaned material. At a life of approximately 20 hours the curves cross, and the precleaned material appears to have a slight strength advantage. There was, however, only a small difference in strength at the 100-hour level, and the values obtained were only slightly above that of unalloyed tungsten.

The tensile or 0.1-hour stress-rupture strengths of these two tungsten-zirconia materials were appreciably higher than that of unalloyed tungsten. In addition, the material without hydrogen precleaning was superior in tensile strength to the best of the tungsten-hafnia materials, that is, 39 300 against 30 100 psi. The relatively rapid decrease in strength with time indicated by comparison of the tensile and 100-hour strengths is further emphasized by the extrapolated life at 3000^o F and 8000 psi of only 32 to 52 hours (fig. 9).

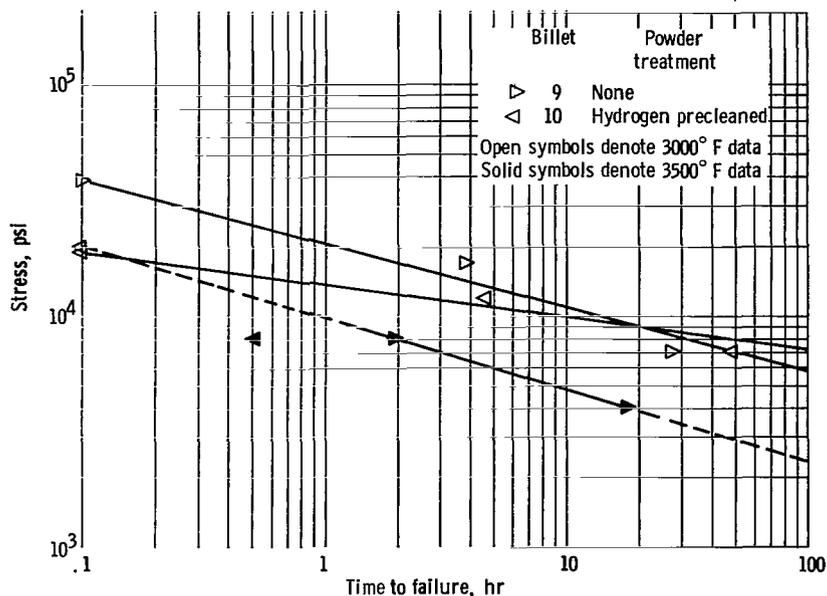


Figure 5. - Stress-rupture strength of tungsten - 5 volume percent zirconium oxide composites. Reduction ratio, 12:1; extrusion temperature, 4000° F.

Two specimens of the uncleaned material were available for testing at 3500° F. As can be seen in figure 5, the slope of the line connecting these test points was approximately equal to that of the 3000° F test. Extrapolating back to the 0.1-hour rupture strength gives a value that is approximately equivalent to the 3000° F strength of the hydrogen precleaned material.

Table V indicates that the ductility of the zirconia-containing composites was lower than that of the hafnia materials. Both the elongation and reduction-in-area values fell below those of unalloyed tungsten. As with the hafnia composites, there appeared to be no direct correlation between ductility and strength.

Tungsten plus thoria: The stress-rupture strength values obtained for the tungsten-thoria composites were exceptionally low even when compared with values for unalloyed tungsten. As a result, no attempt was made to present this data graphically. The actual test results, however, are given in table V.

Tungsten plus zirconium. - Tensile and stress-rupture strength data obtained from specimens produced from two different nominal tungsten - 0.5 weight percent zirconium powders are shown in figure 6. Of the two billets prepared from powder produced by coprecipitation and reduction of mixed oxides, one received a hydrogen precleaning treatment prior to consolidation. The effect of this treatment was similar in nature to that observed for the tungsten-zirconia composites described previously; that is, pre-cleaning in hydrogen resulted in lower strength values. In contrast to the zirconia-containing materials, however, there was no crossover point where the precleaned ma-

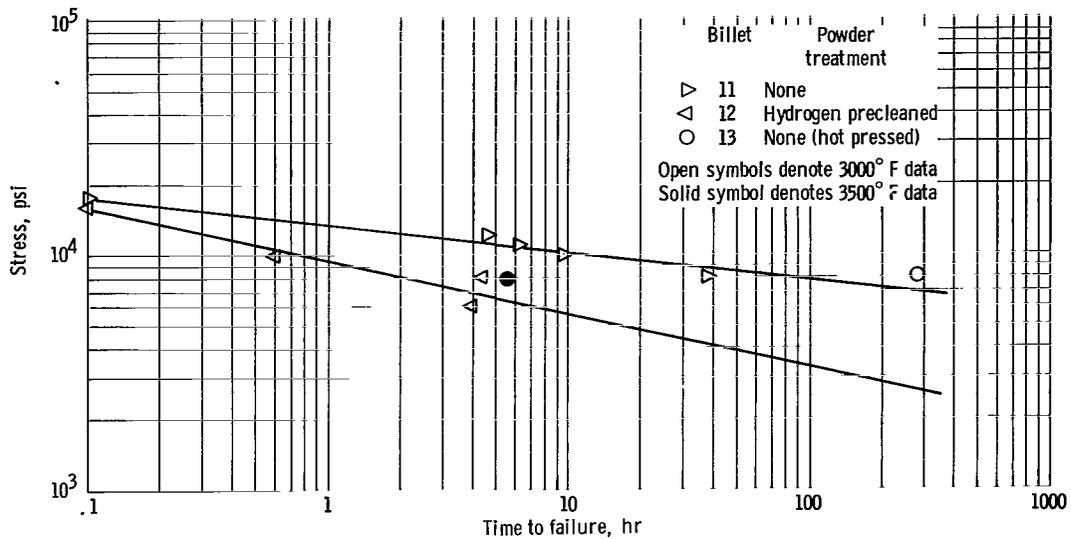


Figure 6. - Stress-rupture strength of tungsten - 0.5 weight percent zirconium. Reduction ratio, 12:1; extrusion temperature, 4000° F.

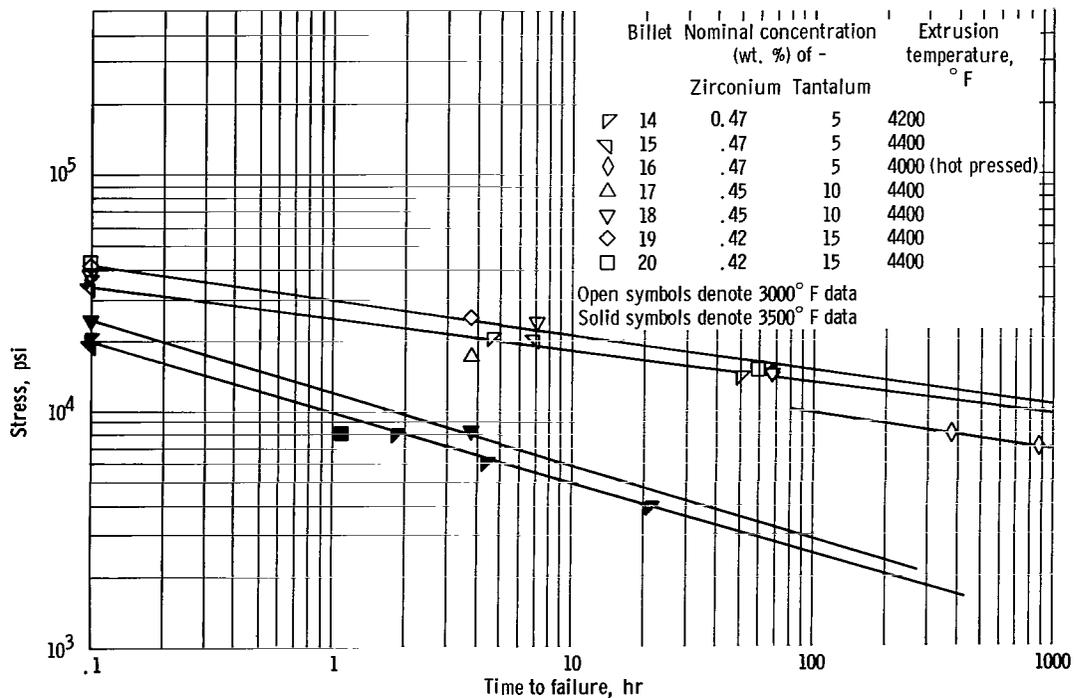


Figure 7. - Stress-rupture strength of tungsten plus zirconium and tantalum composites. Reduction ratio, 12:1.

terials were stronger. At the shorter test times both billets yielded specimens possessing roughly equivalent strengths. At 100 hours, however, the uncleaned material exhibited a rupture strength of about 7600 psi, whereas the precleaned material was lower in strength than unalloyed tungsten (fig. 8).

The billet prepared from powder derived from arc-melted tungsten-zirconium was difficult to extrude and machine; consequently, only two specimens were available for testing. At 3000^o F the stress-rupture life at a stress of 8000 psi was 283 hours. As can be seen in figure 6, this value is slightly above the extension of the curve for the uncleaned coprecipitated material. When the test temperature was increased to 3500^o F, the life of this material under the same load decreased to 5.5 hours. Figure 9 reveals, however, that this life value is greater than that for the precleaned coprecipitated material at 3000^o F (2.2 hr) and slightly exceeds the 3500^o F life of the tungsten-hafnia composite extruded at 16:1 (4.8 hr).

Reduction-in-area and elongation measurements for specimens from the three tungsten-zirconium billets revealed that the uncleaned coprecipitated material was very ductile (up to 100 percent reduction in area). The values obtained were in fact generally superior to those of unalloyed tungsten over the range of times and stresses studied. Both the precleaned material and the originally arc-melted material (consolidated by hot pressing) exhibited a much lower ductility (table V).

Tungsten plus zirconium and tantalum. - The addition of 5 to 15 percent by weight of tantalum powder to the nominal tungsten - 0.5 weight percent zirconium materials produced by coprecipitation and reduction resulted in a substantial increase in strength properties; however, as shown in table V and presented graphically in figure 7, increasing the tantalum content from 5 to 15 weight percent did not significantly influence the actual strength level achieved. At a life of 100 hours and 3000^o F the rupture strengths ranged from 13 200 to 15 000 psi. This represents a slight strength advantage relative to the tungsten-hafnia extruded at 16:1 and is generally considerably better than the other tungsten-base composites studied (fig. 8). A similar strength improvement was also noted in the tensile or 0.1-hour rupture strengths. One of the specimens containing the nominal 15-weight-percent tantalum addition exhibited a 3000^o F tensile strength of greater than 40 000 psi. Despite the generally superior strengths obtained in the time interval of 0.1 to 100 hours, the stress-rupture lives at 3000^o F and 8000 pounds per square inch extrapolated to values below those of the best tungsten-hafnia materials (fig. 9).

Only one of the tungsten plus zirconium and tantalum composites yielded sufficient material for extensive testing at 3500^o F. The stress-rupture curve for this composite (tungsten - 0.47 weight percent zirconium and 5 weight percent tantalum) is included in figure 7. Although the 3500^o F tensile or 0.1-hour stress-rupture strength of this

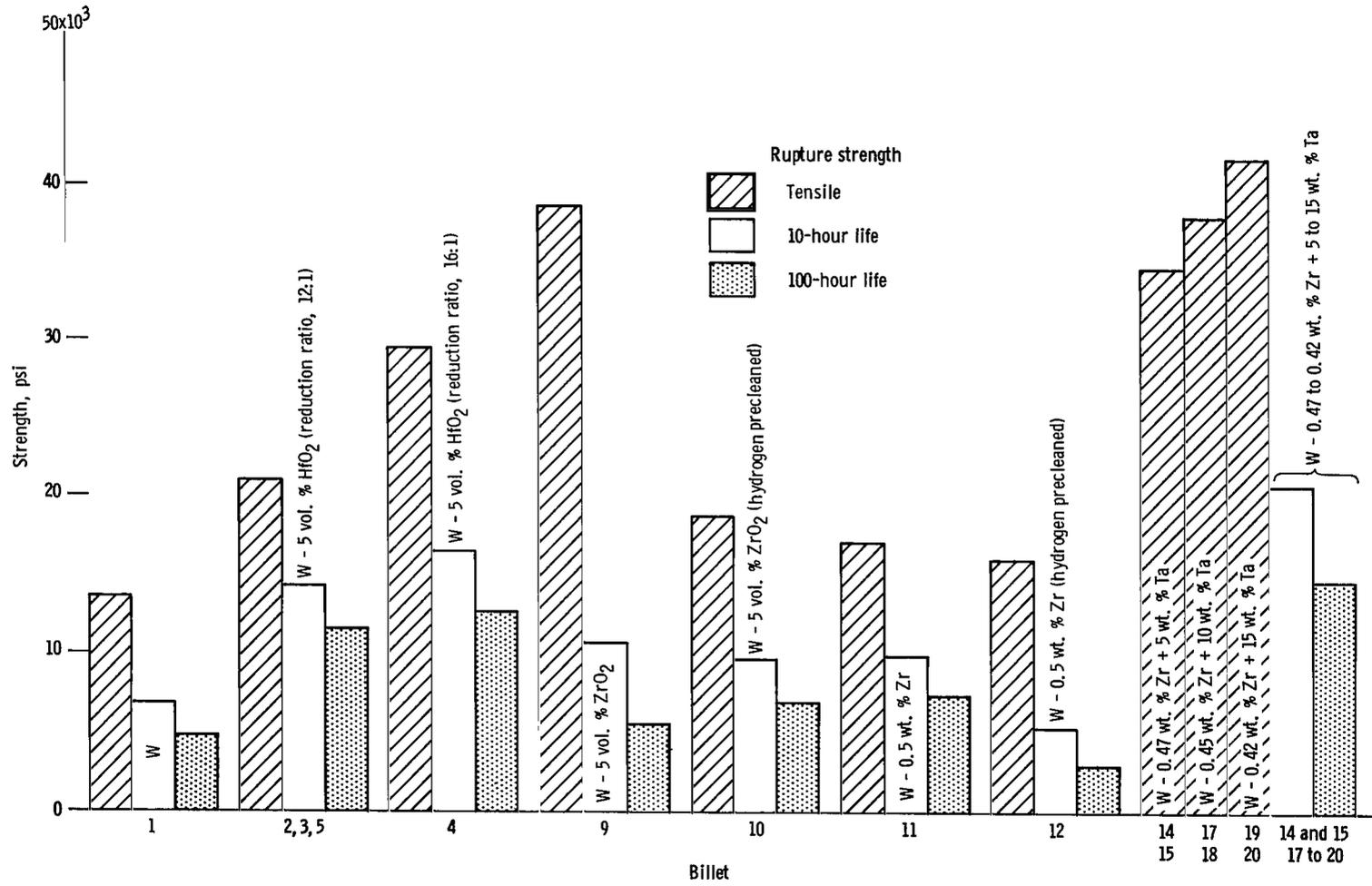


Figure 8. - Tensile, 10-, and 100-hour rupture strengths of tungsten and tungsten-base composites. Test temperature, 3000° F.

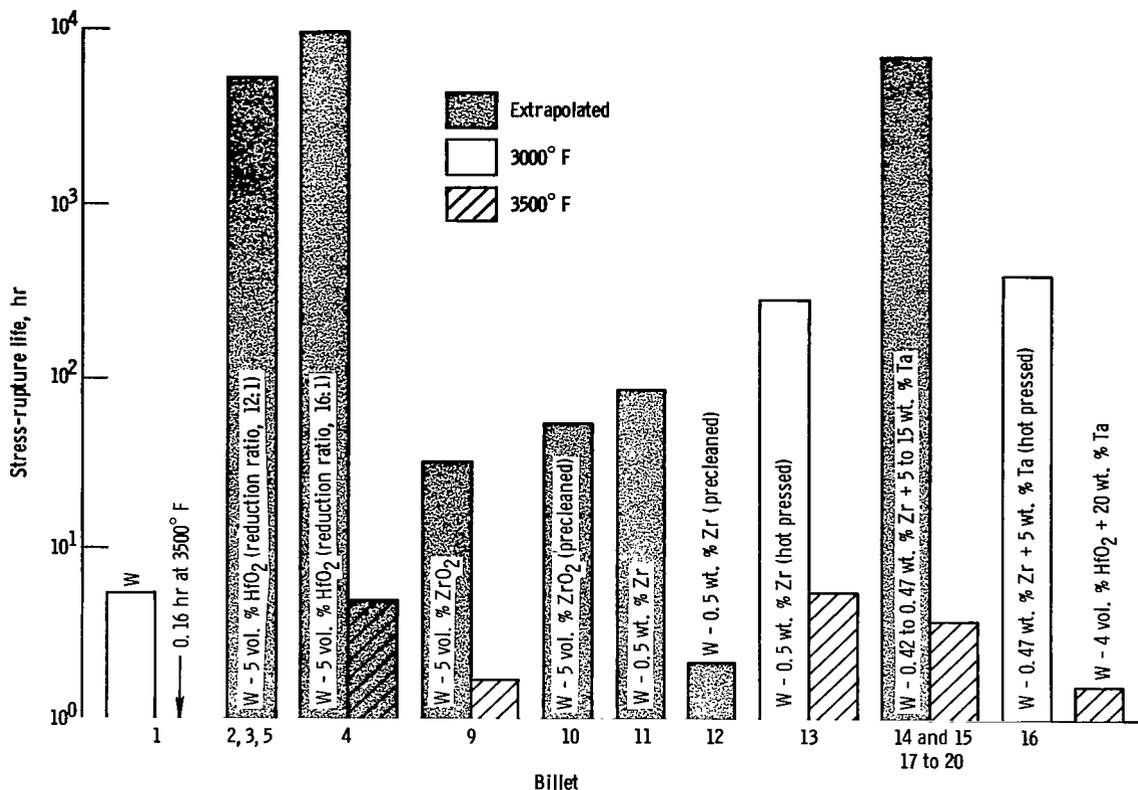


Figure 9. - Stress-rupture life of tungsten and tungsten-base composites. Stress, 8000 psi.

material (20 600 psi) was roughly equivalent to the lower level of strengths observed for this series of materials at 3000⁰ F, the slope of the 3500⁰ F curve is steeper. At 3500⁰ F and 8000 pounds per square inch, the rupture lives of all of these composites fell within the range of 1.2 to 3.8 hours.

The ductility of the tungsten plus zirconium and tantalum composites produced from powders prepared by coprecipitation and reduction exhibited a large amount of scatter. Although one specimen had a measured fracture elongation of 48 percent, most of the values for both elongation and reduction in area were generally considerably below those of unalloyed tungsten (table V).

The use of arc-melted and comminuted tungsten - 0.5 weight percent zirconium in combination with 5 weight percent tantalum also resulted in a relatively high-strength material. At 3000⁰ F, the 100-hour stress-rupture strength was approximately 9800 psi. At the same temperature and a stress of 8000 psi the rupture life was 379 hours, as compared with 283 hours for the same material without tantalum. Note that both of these values represent actual test data, whereas most of the results for the other composite materials were obtained by extrapolation. As with the composites based on the coprecipitated and reduced tungsten-zirconium, the ductility of this material was quite low.

Tungsten plus oxides and tantalum. - Tungsten-plus-oxide-and-tantalum composites were prepared from powder blends containing a 20 weight percent tantalum addition to the tungsten-plus-oxide powders prepared by coprecipitation and selective reduction.

Five billets were prepared: two based on tungsten-hafnia, two based on tungsten-zirconia, and one based on tungsten-thoria. Only the two containing hafnium oxide yielded any material suitable for testing. Even in this case the extrusions were severely cracked, and only a limited number of tests could be performed. The results shown in table V and figure 9 indicate that this combination with tantalum at the 20 weight percent level did not produce a strong material.

Density

The calculation of percent theoretical density depends on a knowledge of the chemical

TABLE VI. - CHEMICAL ANALYSIS AND THEORETICAL DENSITY OF EXTRUDED MATERIALS

[Carbon content determined by combustion with chromatographic technique; oxygen by inert gas fusion; all others by semiquantitative spectrographic analysis.]

Billet	Nominal analysis, weight percent	Actual chemical analysis, weight percent									Theoretical density, g/cu cm
		C	O ₂	H _f	H _f O ₂	Th	ThO ₂	Zr	ZrO ₂	Ta	
1	Tungsten	0.025	0.08	NA ^a	NA	NA	NA	NA	NA	NA	19.35
2	2.8 Hafnia	.013	.22	1.22	1.35	↓	↓	↓	↓	↓	18.99
3	2.8 Hafnia	.020	.06	1.44	.87	↓	↓	↓	↓	↓	19.06
4	2.8 Hafnia	.029	.14	1.18	.91	↓	↓	↓	↓	↓	19.07
5	2.8 Hafnia	.009	.32	.54	2.09	↓	↓	↓	↓	↓	18.91
7	2.7 Thoria	.003	.04	NA	NA	2.14	0.20	↓	↓	↓	19.05
8	2.7 Thoria	.002	.05	↓	↓	1.83	.24	↓	↓	↓	19.08
9	1.7 Zirconia	.009	.18	↓	↓	NA	NA	0.07	0.69	↓	19.02
10	1.7 Zirconia	.010	.34	↓	↓	↓	↓	.82	.05	↓	19.02
11	0.5 Zirconium	.0004	.31	↓	↓	↓	↓	.25	.65	↓	18.89
12	0.5 Zirconium	.0005	.14	↓	↓	↓	↓	.01	.55	↓	19.13
13	0.5 Zirconium	.012	.01	↓	↓	↓	↓	.56	.04	↓	19.12
14	0.47 Zirconium + 5.0 tantalum	.016	.30	↓	↓	↓	↓	.64	1.00	4.90	18.59
15	0.47 Zirconium + 5.0 tantalum	.012	.29	↓	↓	↓	↓	.99	1.12	4.93	18.37
16	0.47 Zirconium + 5.0 tantalum	.095	.05	↓	↓	↓	↓	.07	.20	4.57	19.09
17	0.45 Zirconium + 10.0 tantalum	.026	.27	↓	↓	↓	↓	.70	1.18	9.86	18.31
18	0.45 Zirconium + 10.0 tantalum	.010	.25	↓	↓	↓	↓	1.49	.33	9.85	18.37
19	0.42 Zirconium + 15 tantalum	.009	.21	↓	↓	↓	↓	1.62	.81	13.02	18.04
20	0.42 Zirconium + 15 tantalum	See table VII									
28	2.24 Hafnia + 20 tantalum	.019	.26	.71	1.51	NA	NA	NA	NA	NA	-----
29	2.24 Hafnia + 20 tantalum	.016	.27	1.37	1.76	NA	NA	NA	NA	17.78	17.78

^aNot analyzed.

TABLE VII. - CHEMICAL ANALYSES AND THEORETICAL
 DENSITIES OF NOMINAL TUNGSTEN - 0.42 WEIGHT
 PERCENT ZIRCONIUM PLUS 15 WEIGHT PERCENT
 TANTALUM COMPOSITE (BILLET 20)

Sample	Zirconium	Zirconia	Tantalum	Theoretical density, g/cu cm
1	0.40	0.95	10.98	18.44
2	.53	.08	13.49	18.70
3	1.40	.49	12.25	18.25
4	NA ^a	NA	12.81	-----

^aNot analyzed.

analysis of the material in question. As a first approximation, a set of density values was determined based on the nominal analysis of the starting materials. When these calculated values were compared with the measured densities, all the materials were noted to be greater than 98 percent of theoretical density. As shown in table V, some composites exhibited densities in excess of 100 percent of theoretical. New values of the theoretical densities of the composites were calculated based on chemical analyses (table VI). All the materials again appeared to be greater than 98 percent dense. In addition, however, a considerably greater number of the composites seemed to possess densities in excess of 100 percent of theoretical (table V). At this point several check analyses were run by different analytical laboratories. The results shown in table VII demonstrate the variation in reported analysis for a nominal tungsten - 0.42 weight percent zirconium plus 15 weight percent tantalum composite. In view of the apparent inability to obtain consistent chemical analyses even for major elements, no further attempts were made to calculate a more precise theoretical density for the various composites. Thus, the densities in all cases were merely assumed to be quite close to theoretical.

Lattice Parameters

Lattice parameter determination for the tungsten used as a standard indicated a cubic spacing of 3.167 angstroms. This value compares favorably with the American Society for Testing Materials (ASTM) standard value for tungsten of 3.165 angstroms. The tungsten-plus-oxide composites containing either hafnia, zirconia, or thoria at the 5 volume percent level produced from powders prepared by coprecipitation and selective reduction yielded values varying between 3.162 to 3.167 angstroms. The composite pre-

pared from powders derived from an originally arc-melted tungsten - 0.5 weight percent zirconium ingot exhibited a spacing of 3.170 angstroms, whereas the coprecipitated and reduced powder of the same composition yielded values of 3.163 to 3.164 angstroms.

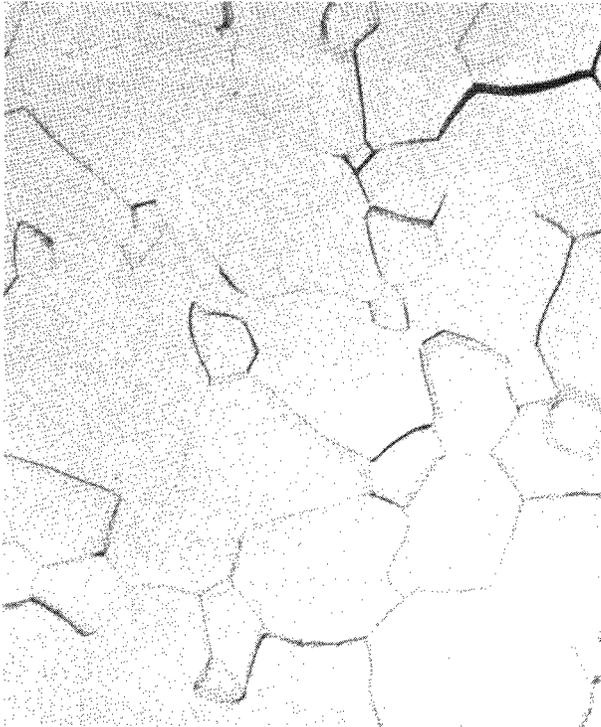
Incorporation of 5 to 15 weight percent tantalum in the nominal tungsten - 0.5 weight percent zirconium matrix resulted in lattice parameters that ranged from 3.172 to 3.184 angstroms. The spread in values, as is shown in table V, is independent of tantalum content. The values obtained, however, signify an expansion of the tungsten lattice indicative of solid solution alloying. One of the tungsten-plus-oxide-and-tantalum composites (tungsten - 5 volume percent hafnia plus 20 weight percent tantalum) was also evaluated and found to have a spacing of 3.188 angstroms.

Hardness

The diamond-pyramid hardness (table V) for as-extruded unalloyed tungsten was 372 in the longitudinal and 371 in the transverse direction. The composites exhibited hardness values in the longitudinal and transverse directions that ranged from 359 to 477 and 369 to 497, respectively. In general, higher hardness readings were obtained with the tantalum-bearing materials than with those composites containing only oxides or zirconium. The highest hardness measured (497) occurred in the transverse cross-section of the tungsten - 0.42 weight percent zirconium plus 15 weight percent tantalum composite extruded in a molybdenum can. Almost all of the high-strength materials had diamond pyramid hardnesses above 380, but there was no consistent correlation between hardness and strength. Furthermore, differences were noted in some cases between the longitudinal and transverse hardness even though in most instances the grain diameters were nearly equivalent in both directions.

Grain Size

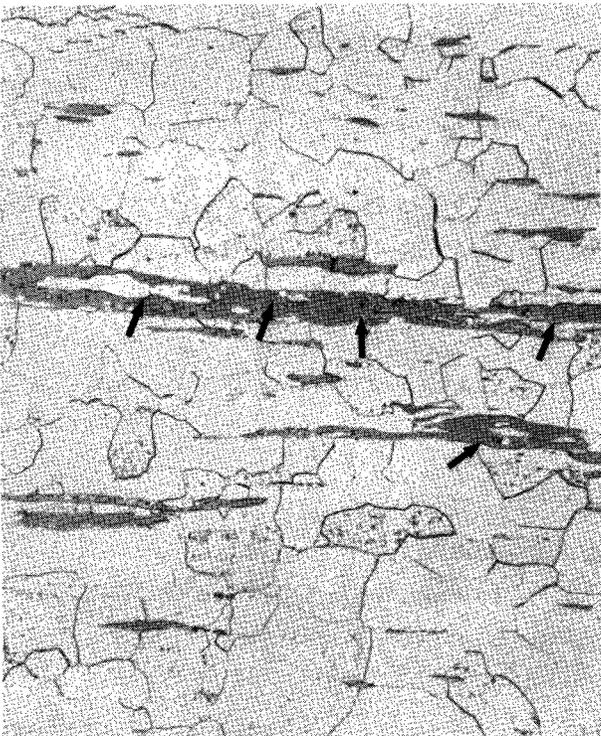
The average grain diameter for the unalloyed tungsten was 0.0025 and 0.0022 centimeter in the longitudinal and transverse directions (table V). With additives, the average grain diameter ranged from 0.0004 to 0.0044 centimeter. In general very little variation existed between the longitudinal and transverse grain size. Although a majority of the higher strength materials possessed the finer grain sizes no consistent correlation between grain size and strength properties was evident.



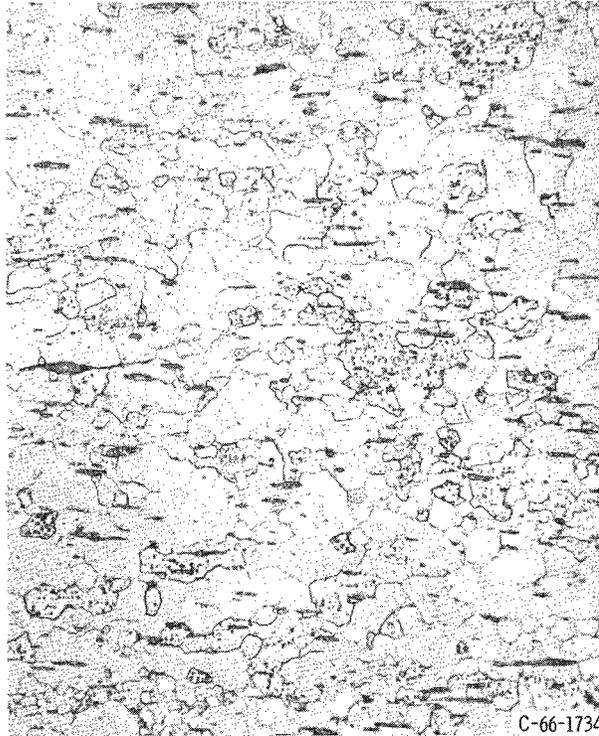
(a) Unalloyed tungsten (billet 1). Extrusion temperature, 3800° F.



(b) Tungsten-hafnia (billet 3). Extrusion temperature, 4000° F.



(c) Tungsten-zirconia (billet 10). Extrusion temperature, 4000° F.
(Note arrows indicating globular constituent.)



(d) Tungsten-thoria (billet 7). Extrusion temperature, 4200° F.

Figure 10. - Structures of as-extruded tungsten and tungsten - 5 volume percent oxide composites. Reduction ratio, 12:1; longitudinal sections; etchant, Murakami's reagent. X500.

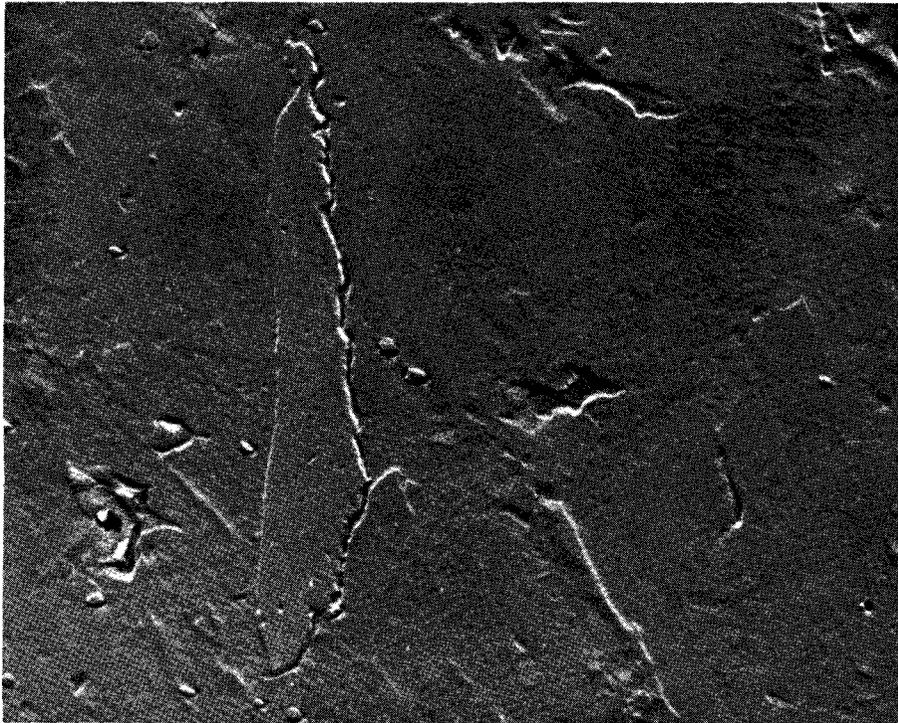
Microstructure

Photomicrographs of typical longitudinal cross sections of the as-extruded materials are presented. Note that all the materials exhibited essentially equiaxed grains despite the fact that a relatively high reduction ratio (12:1) was utilized. Selected areas of many of the composites were also examined by electron microscopy.

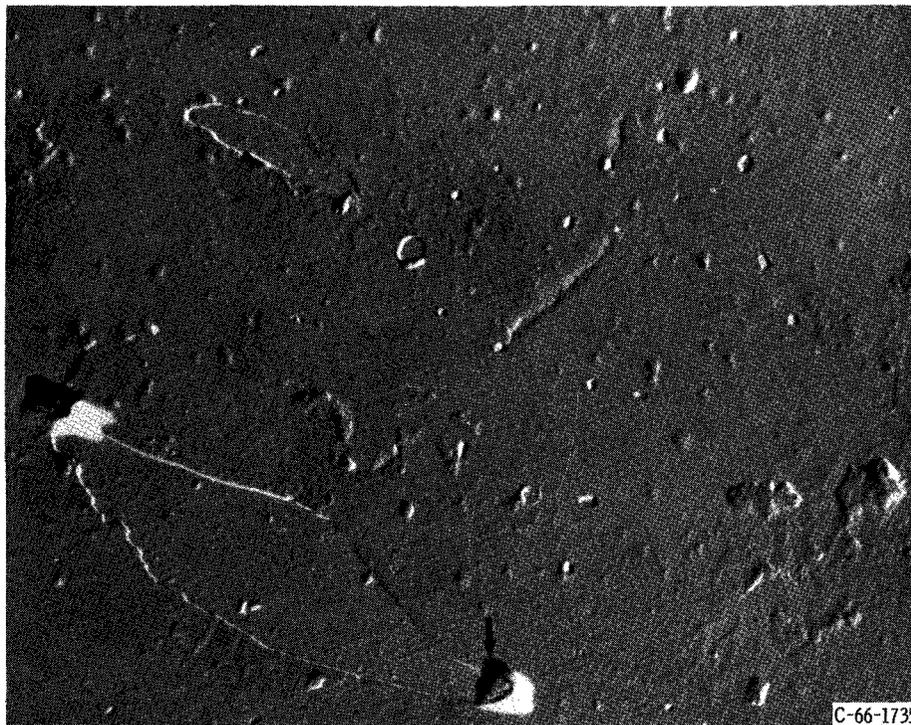
Tungsten plus oxides. - Figures 10(a) to (d) show the structures obtained with the tungsten standard and the tungsten-plus-oxide composites. Examination of these photomicrographs reveals the presence of agglomerated and elongated oxides, with very little evidence of any fine dispersoids except perhaps for the tungsten-thoria composite (fig. 10(d)).

Examination of the microstructure of the tungsten-hafnia and tungsten-zirconia composites at 10 000 to 30 000 revealed the presence of a nonuniform distribution of relatively fine dispersoids located in the areas between the large elongated oxides. For the tungsten-hafnia composites the particle size range of these finer oxides was generally 0.03 to 0.8 micron (fig. 11(a)); with the tungsten-zirconia, where there were more fine particles, the range was 0.06 to 0.3 micron (fig. 11(b)). In the latter case, most of the particles were less than 0.1 micron. Both these materials exhibited some evidence of microporosity in the areas adjacent to and contiguous with the elongated oxides. This microporosity was particularly prevalent with the tungsten-zirconia. Although it is not evident from figure 11, a greater number of the finer particles were present in the tungsten-thoria than in either of the other two tungsten-plus-oxide composites. In addition, with thoria, two distinct particle-size ranges were noted. The smaller particles were generally less than 0.03 to 0.3 micron, while the larger ones were approximately 0.5 to greater than 3 microns (fig. 11(c)). Relatively little indication of elongation was present in most of the particles, and the matrix, although generally quite dense, appeared to contain considerable evidence of microporosity.

Tungsten plus zirconium. - Photomicrographs of tungsten plus 0.5 weight percent zirconium prepared from two different starting materials and by two different consolidation methods are shown in figures 12(a) and 13(a). Coprecipitated and reduced powder consolidated by cold pressing and duplex sintering (fig. 12(a)) exhibited a relatively clean tungsten matrix with a small number of severely elongated oxides. At X500 no evidence of any fine dispersoids was present. Electron micrographs of this material at 10 000 to 30 000 once again reveal the presence of fine dispersoids in the areas between the large fibered oxides. The size range of these dispersoids was generally 0.03 to 0.2 micron, and they were relatively uniformly distributed (fig. 14(a)). Voids and microporosity were also noted. Unlike tungsten-zirconia prepared by the same method, however, no evidence of porosity surrounding and contiguous with the large elongated oxides was present.

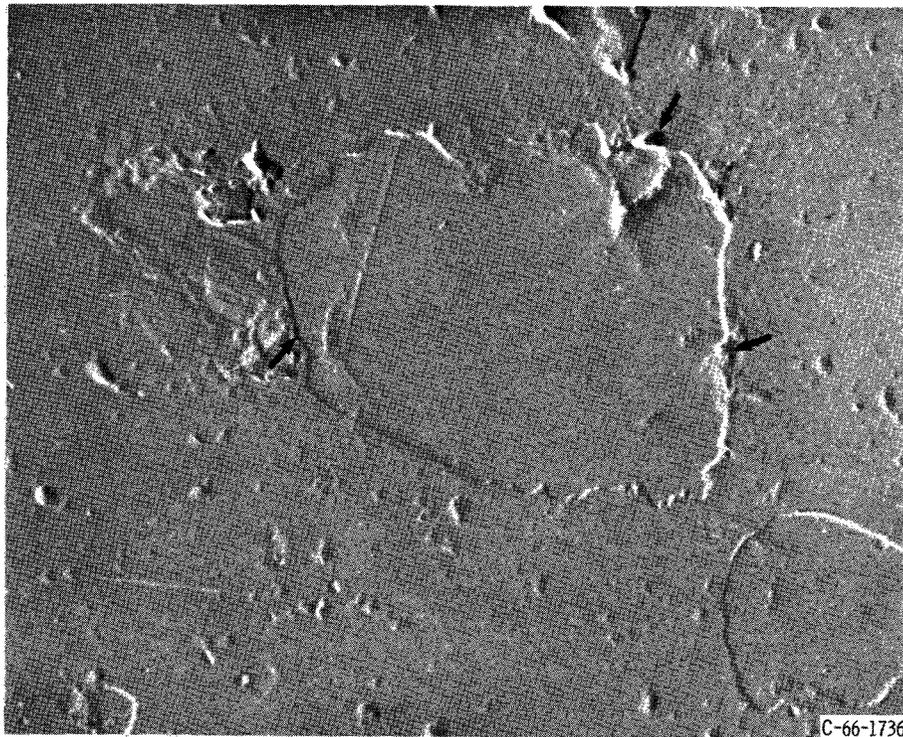


(a) Tungsten-hafnia (billet 3). Extrusion temperature, 4000° F.



(b) Tungsten-zirconia (billet 10). Extrusion temperature, 4000° F.

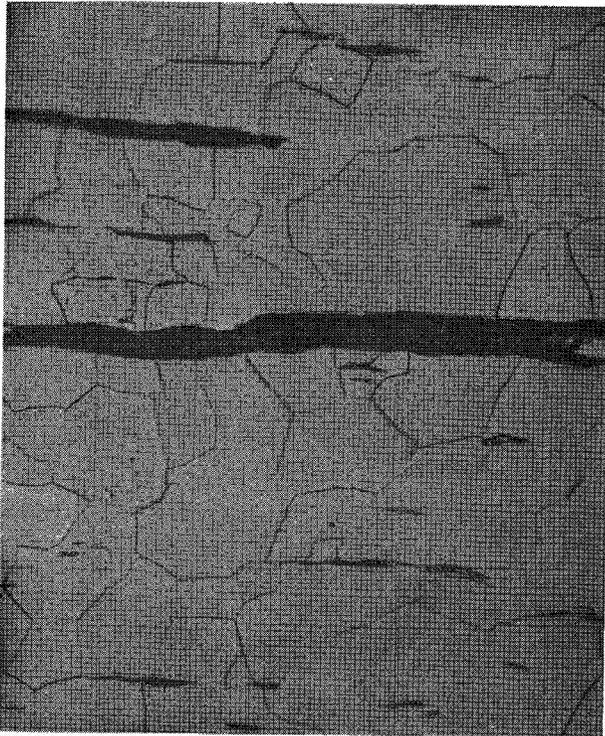
Figure 11. - Structures of as-extruded tungsten - 5 volume percent oxide composites. Reduction ratio, 12:1; longitudinal sections; etchant, 30 percent lactic acid, 10 percent nitric acid, 5 percent hydrofluoric acid. Arrows indicate microporosity. X18 000.



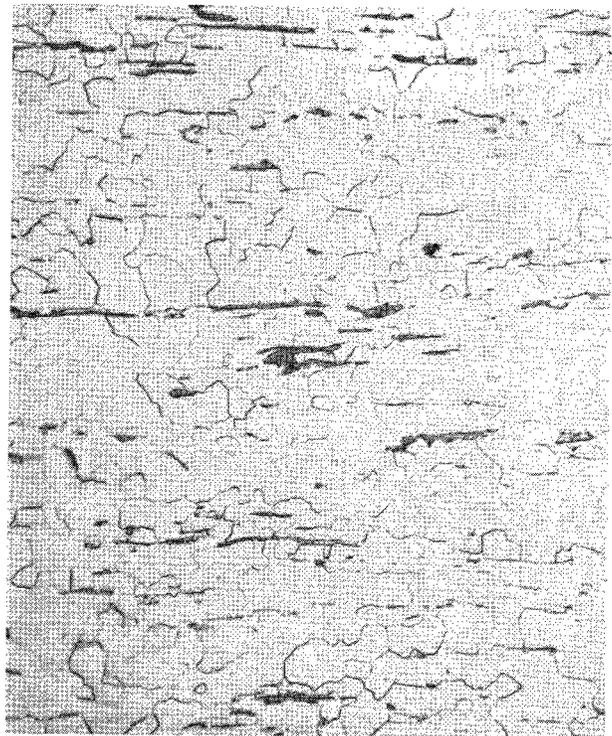
(c) Tungsten-thoria (billet 7). Extrusion temperature, 4200° F.
Figure 11. - Concluded.

Tungsten - 0.5 weight percent zirconium, prepared from an arc-melted and comminuted powder and consolidated by hot pressing, is shown in figure 13(a). The appearance of this material is quite different from that possessing the same nominal composition but prepared by cold pressing and duplex sintering. There were no large elongated particles. The optical micrograph indicates a relatively coarse but uniform distribution of dispersoids. Evidence of segregation of the particles to the grain boundary areas also exists. Examination in the electron microscope at 10 000 to 30 000 confirmed this segregation to the grain boundaries; however, some smaller particles are located within the grains. The range of dispersoid particle sizes in this material was 0.1 to 1.5 microns (fig. 15).

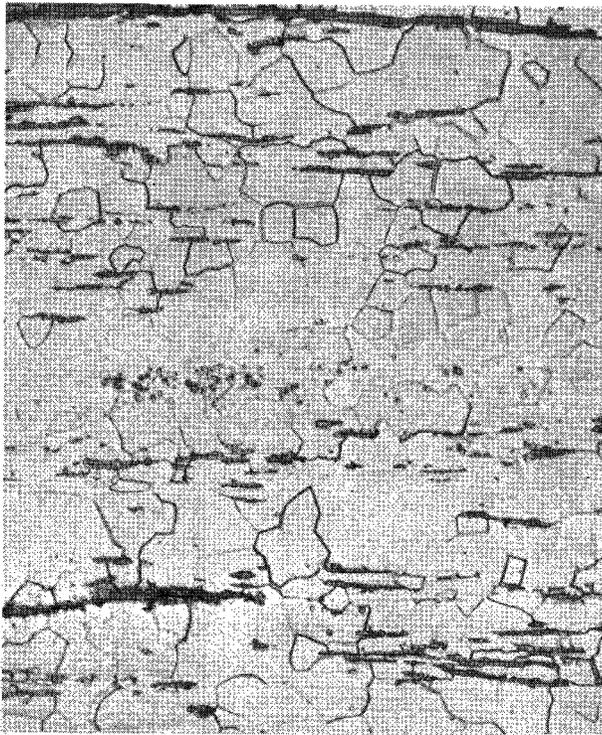
Tungsten plus zirconium and tantalum. - Tantalum additions of 5 to 15 percent by weight to the nominal tungsten - 0.5 weight percent zirconium composites altered the microstructure considerably. The intent of these admixtures of tantalum powder was to form a microstructure in which ductile tantalum-rich zones would alternate with the more brittle tungsten-rich ones. Figures 12(b) to (d) reveal, however, that in most cases the tantalum went completely into solution. Only the composite prepared from the admixture of 5 weight percent tantalum powder to the tungsten - 0.5 weight percent zirconium powder derived from arc-melted tungsten (fig. 13(b)) exhibited any evidence of a two-phase structure.



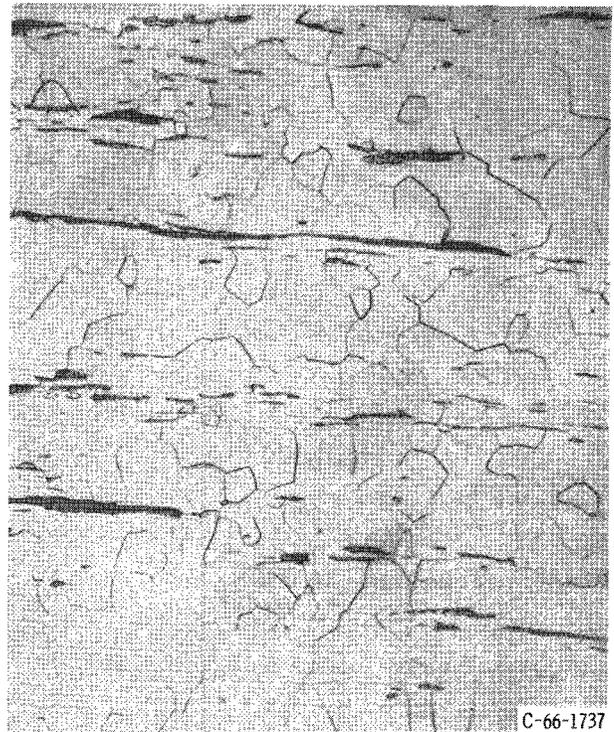
(a) Zero weight percent tantalum (billet 11). Extrusion temperature, 4000° F.



(b) 5 Weight percent tantalum (billet 15). Extrusion temperature, 4400° F.

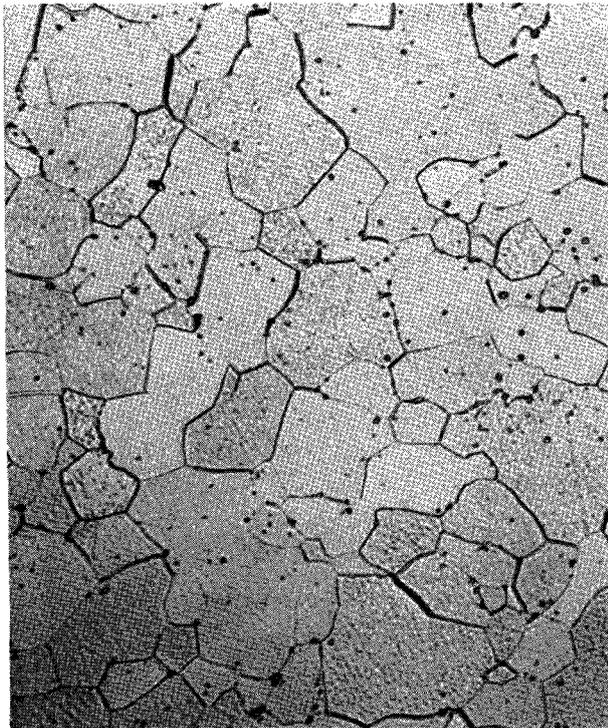


(c) 10 Weight percent tantalum (billet 17). Extrusion temperature, 4400° F.

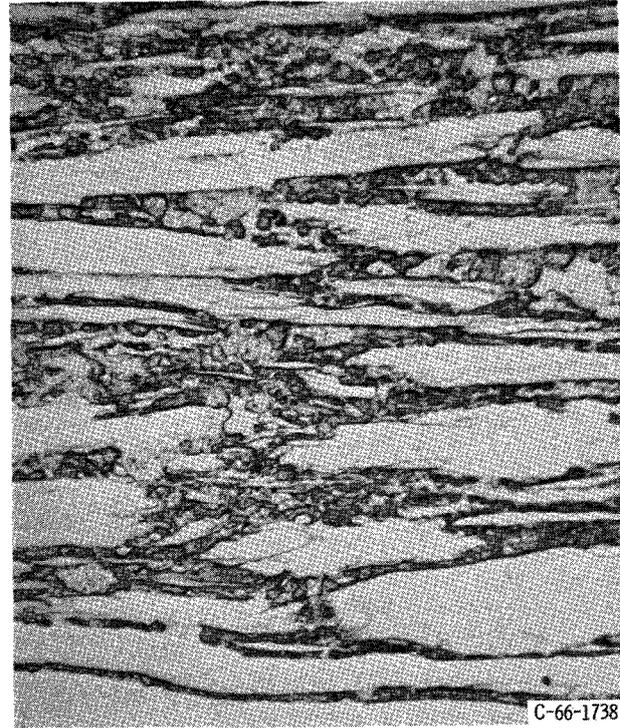


(d) 15 Weight percent tantalum (billet 19). Extrusion temperature, 4400° F.

Figure 12. - Effect of tantalum on as-extruded structure of coprecipitated and reduced tungsten - 0.5 weight percent zirconium. Pressed and sintered; reduction ratio, 12:1; longitudinal sections; etchant, Murakami's reagent. X500.



(a) Zero weight percent tantalum (billet 13). Extrusion temperature, 4200° F.

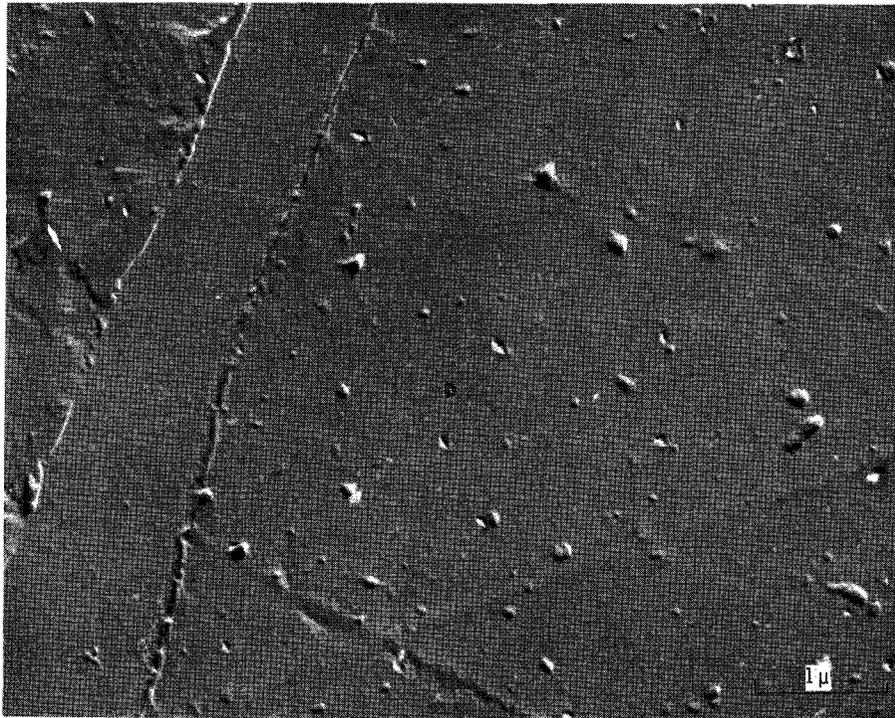


(b) 5 Weight percent tantalum (billet 16). Extrusion temperature, 4000° F.

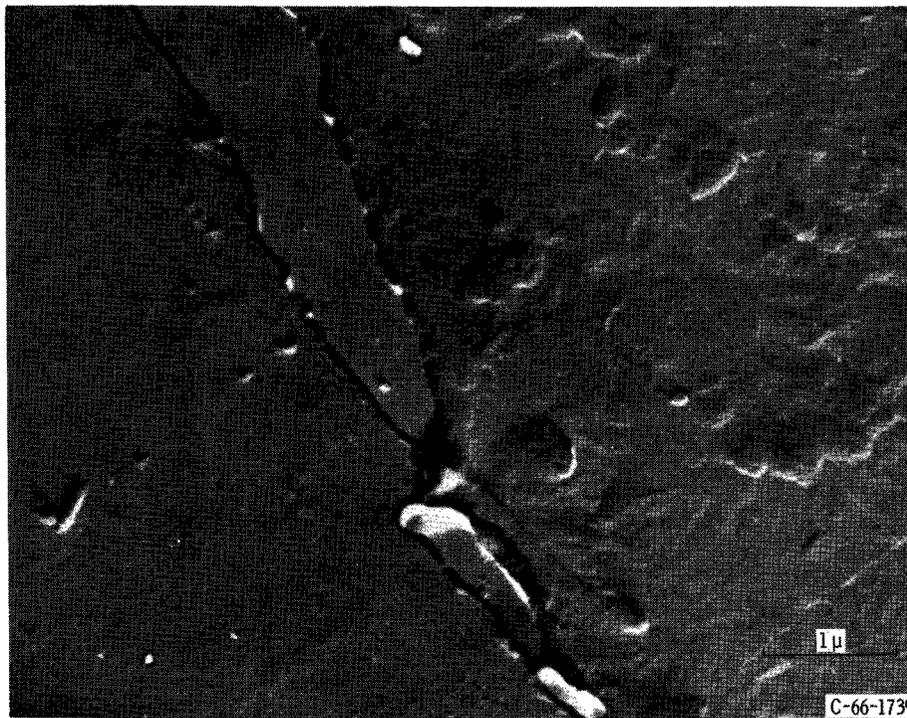
Figure 13. - Effect of tantalum on as-extruded structure of arc-melted and comminuted tungsten - 0.5 weight percent zirconium. Hot pressed; reduction ratio, 12:1; longitudinal sections; etchant, Murakami's reagent. X500.

Typical microstructures obtained with tantalum additions of 5, 10, and 15 percent by weight to the tungsten - 0.5 weight percent powder prepared by coprecipitation and reduction are shown in figures 12(b) to (d). All three of these compositions resulted in relatively equiaxed grain structures with both small and large elongated particles and little indication of any fine dispersoids. Electron micrographs of these same materials at 10 000 to 30 000 revealed a relatively small number of finer dispersoids in the size range of 0.1 to 1 micron (figs. 14(b) to (d)). At these magnifications it also appears that many of the large-fibered particles observed at X500 are in reality composed of more than one particle in close proximity, thus giving rise to the apparently large dispersoid elongations. Some particles also appear to contain flaws and voids parallel to the extrusion direction. In addition the composites containing 15 weight percent tantalum (fig. 14(d)) exhibited large, irregularly-shaped dispersoids with rounded contours. These dispersoids are similar in appearance to the configurations normally observed with liquid phase sintering.

The addition of 5 weight percent tantalum to the tungsten - 0.5 weight percent zirconium powder derived from an originally arc-melted ingot yielded a structure that was



(a) Zero weight percent tantalum (billet 11). Extrusion temperature, 4000° F.

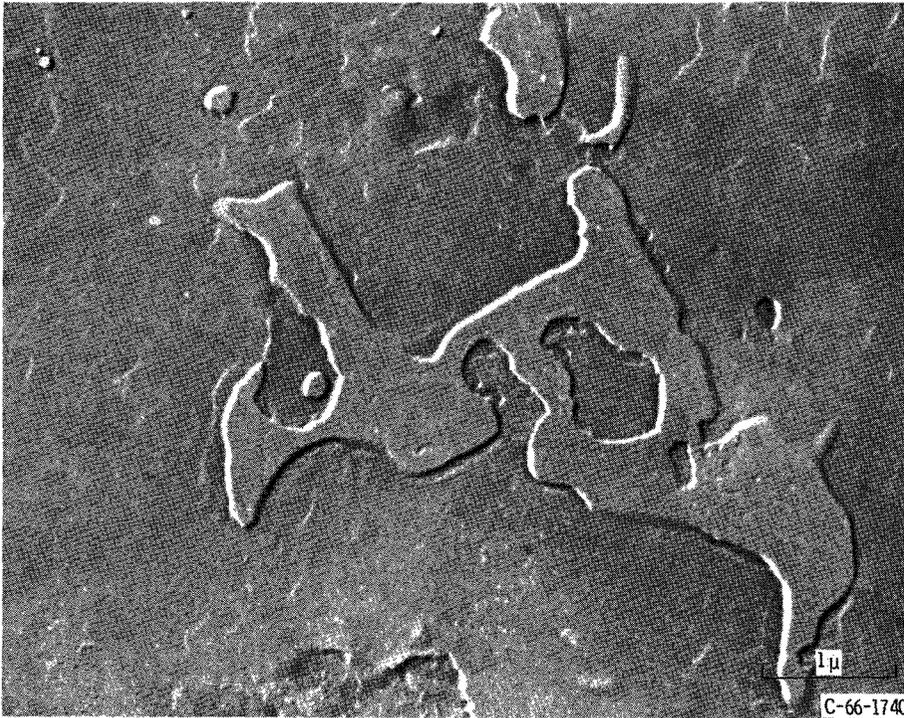


(b) 5 Weight percent tantalum (billet 15). Extrusion temperature, 4400° F.

Figure 14. - Effect of tantalum on as-extruded structure of coprecipitated and reduced tungsten - 0,5 weight percent zirconium. Pressed and sintered; reduction ratio, 12:1; longitudinal sections. Etchant, 30 percent lactic acid, 10 percent nitric acid, 5 percent hydrofluoric acid. X18 000.



(c) 10 Weight percent tantalum (billet 17). Extrusion temperature, 4400° F.



(d) 15 Weight percent tantalum (billet 19). Extrusion temperature, 4400° F.

Figure 14. - Concluded.

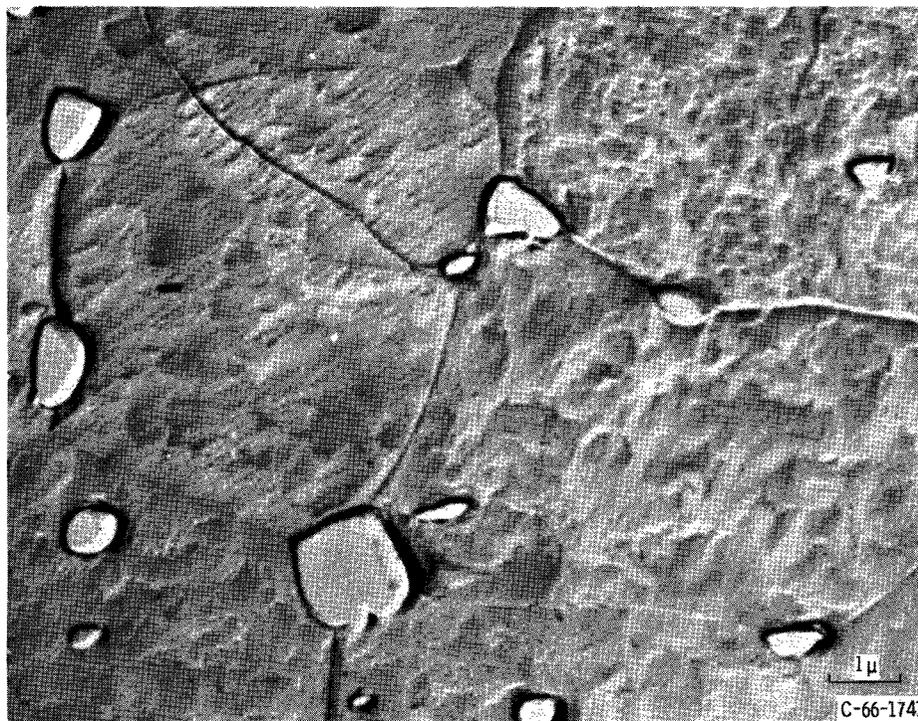
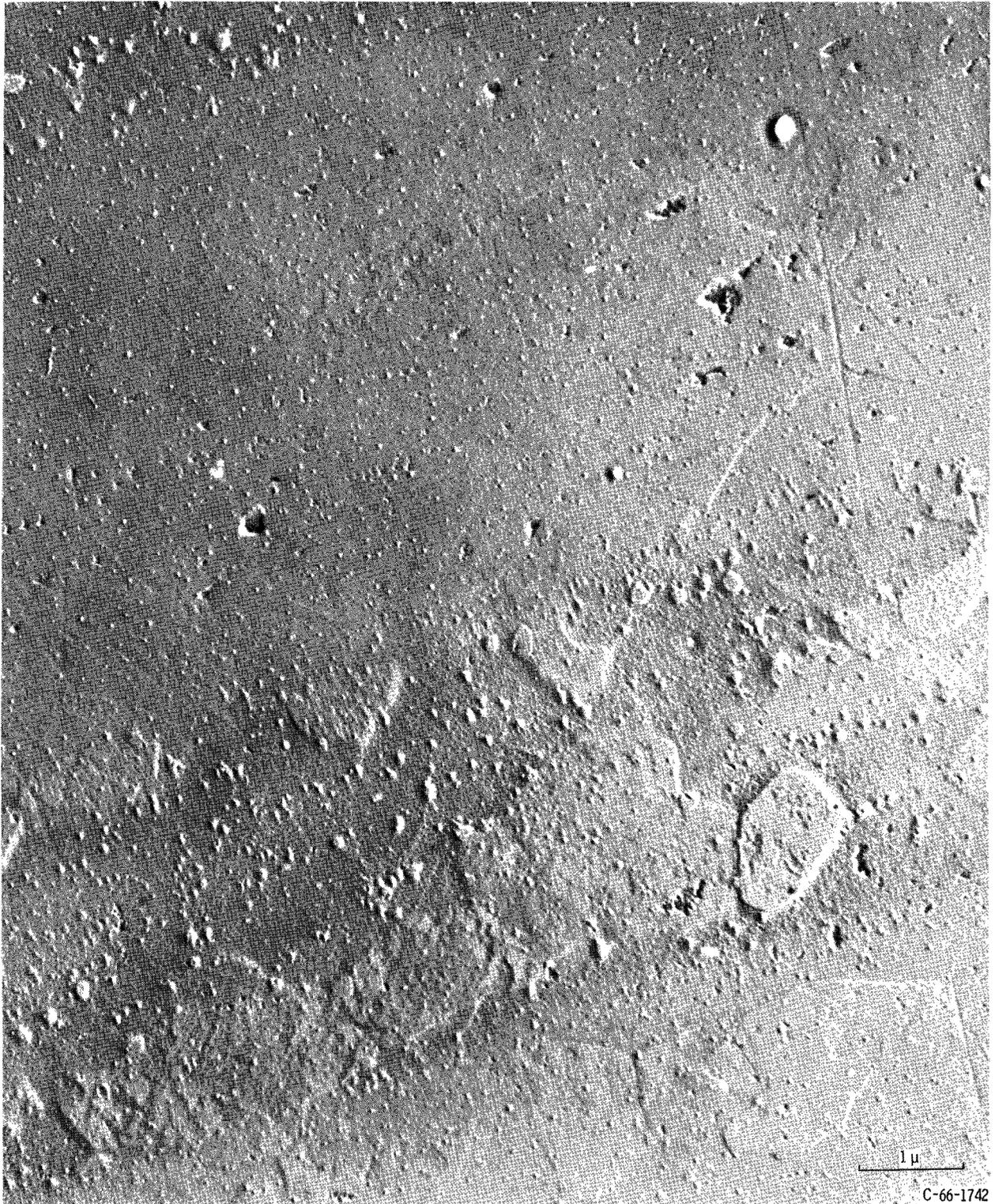


Figure 15. - Structure of as-extruded tungsten - 0.5 weight percent zirconium produced by hot pressing billet 13. Powder prepared by arc-melting and comminution; reduction ratio, 12:1; extrusion temperature, 4200° F; longitudinal section; etchant, Murakami's reagent. X10 000.

considerably different from those described in the preceding paragraphs. The structure of this composite, which was consolidated by hot pressing, is shown in figure 13(b). As noted previously, the structure at X500 contains two distinct phases: an elongated white phase presumably consisting primarily of the tungsten - 0.5 weight percent zirconium constituent surrounded by a darker somewhat globular phase assumed to be primarily tantalum.

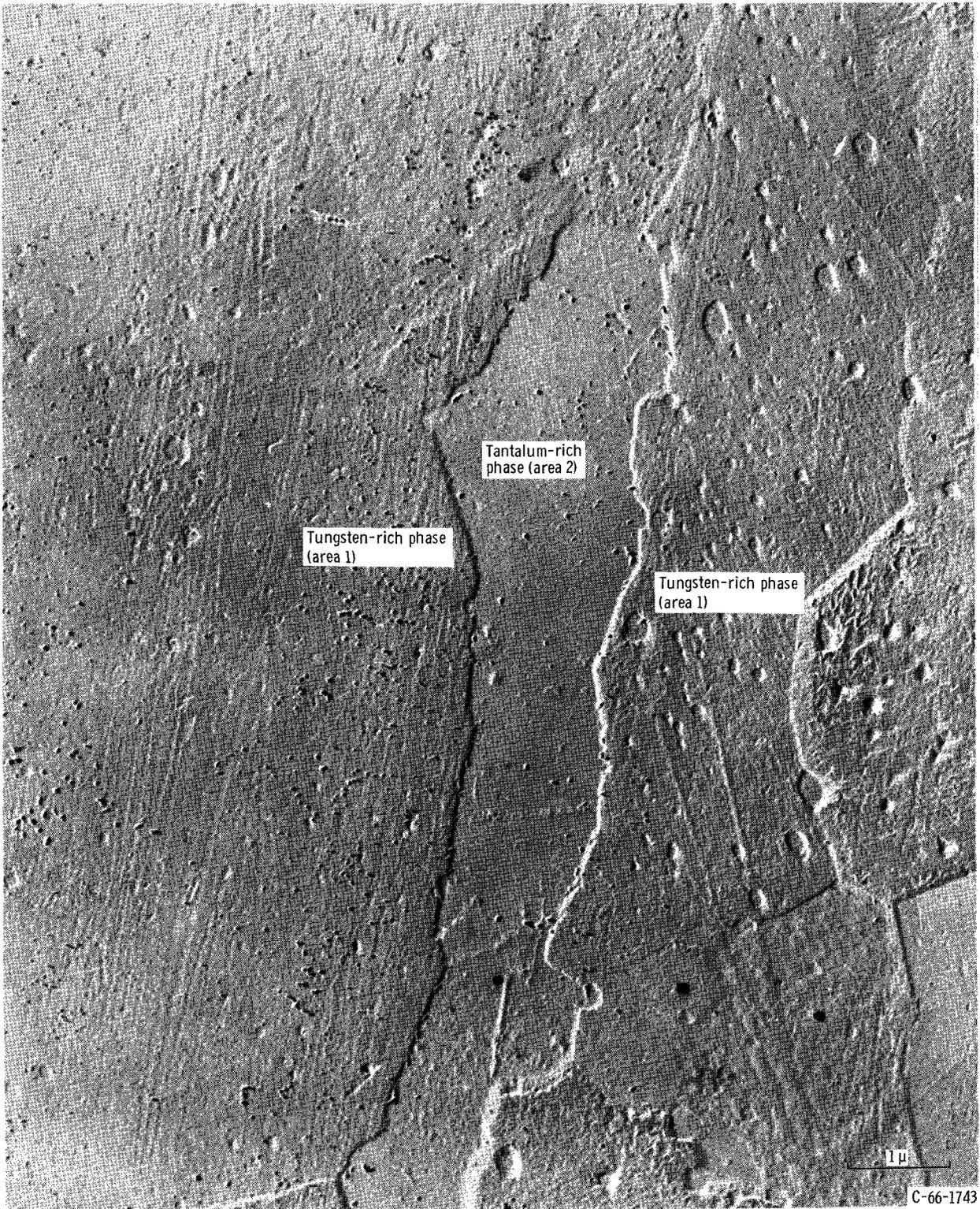
Examination of this same longitudinal cross section by electron microscopy revealed the presence of a uniform distribution of submicron dispersoids throughout the entire matrix (fig. 16(a)). The particle-size range of these dispersoids was 0.03 to 0.4 micron, with a calculated interparticle spacing of 1.90 microns. Etching this structure for tantalum substantiated the presence of two distinct phases; that is, in the electron micrograph of figure 16(b), area 1 corresponds to the lighter etched constituent and area 2 to the darker etched one noted previously in reference to figure 13(b).

In order to gain a clearer understanding of the composition of the two phases as well as to determine, if possible, the chemistry of the dispersoids, a sample of this material was subjected to electron-probe analysis. One channel of the probe was set to record tungsten, the other tantalum. At points where the darker etched constituent was present, the tantalum concentration was at its highest and the tungsten at its lowest. This con-

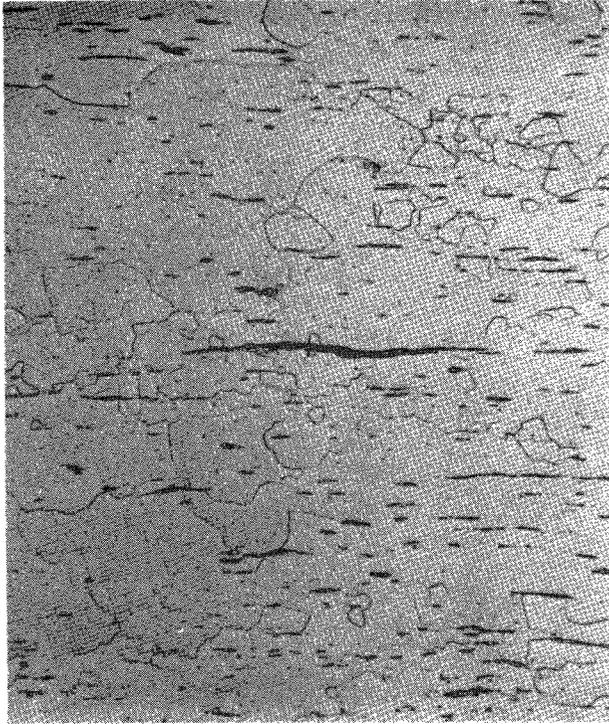


(a) Etched for tungsten. Etchant, 30 percent lactic acid, 15 percent nitric acid, 5 percent hydrofluoric acid.

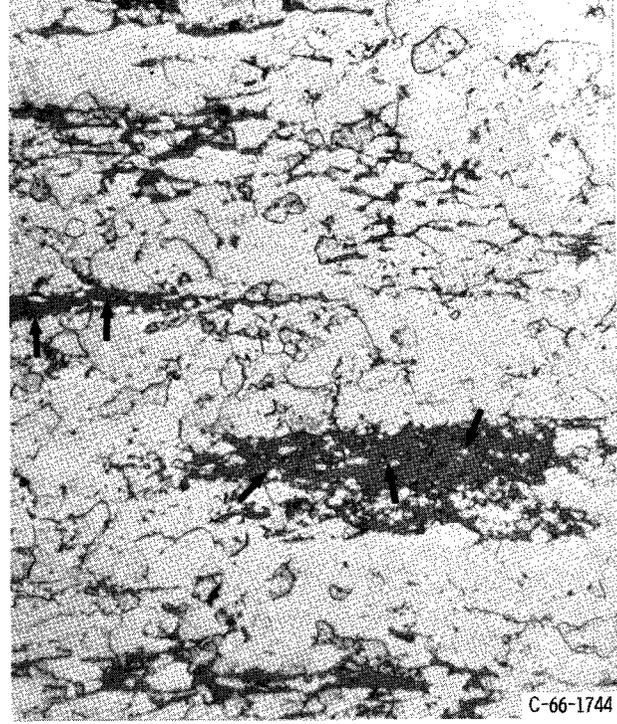
Figure 16. - Structure of as-extruded tungsten-0.5 weight percent zirconium (arc-melted and comminuted) with a 5 weight percent addition of tantalum (billet 16). Hot-pressed; reduction ratio, 12:1; extrusion temperature, 4000° F; longitudinal section. X10 000.



(b) Etched for tantalum. Etchant, 3.5 grams of potassium ferricyanide, 1 gram of sodium hydroxide, 150 milliliters of water.
Figure 16. - Concluded.



(a) Tungsten-hafnia-tantalum (billet 26). Extrusion temperature, 4300° F.



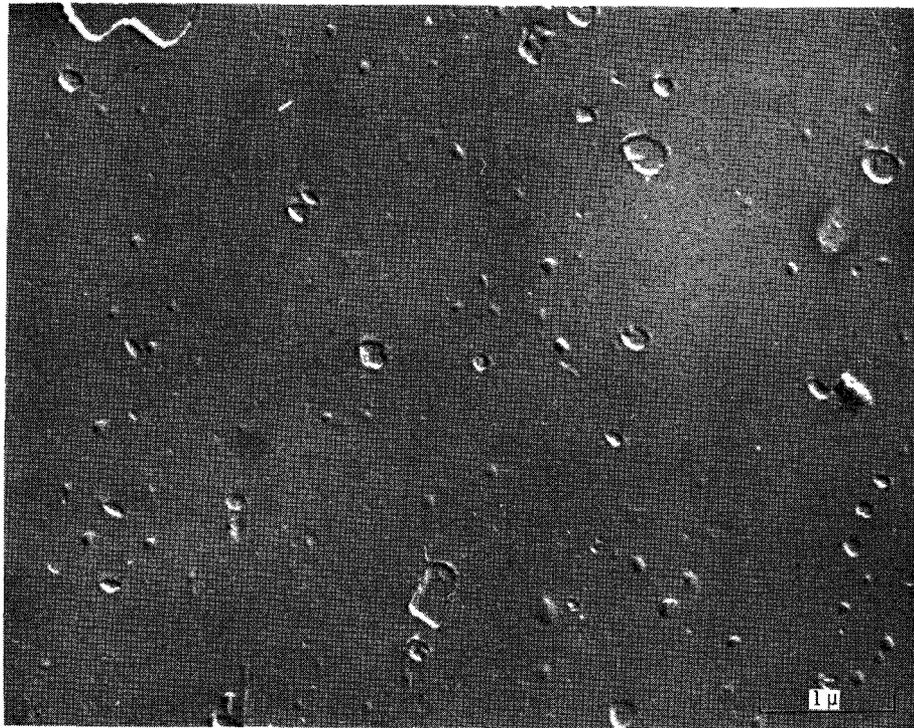
(b) Tungsten-zirconia-tantalum (billet 29). Extrusion temperature, 4000° F. (Note globular constituent arrows.)

Figure 17. - Structures of as-extruded composites based on tungsten - 5 volume percent oxide with 20 weight percent addition of tantalum. Reduction ratio, 12:1; longitudinal sections; etchant, Murakami's reagent. X500.

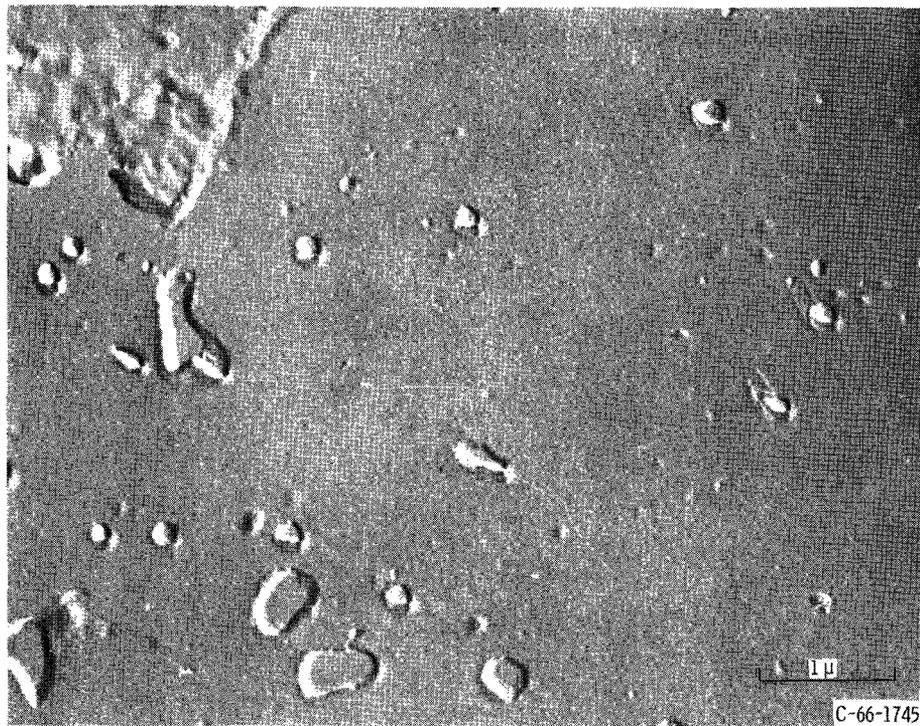
firmed the initial evaluation of the photomicrograph (fig. 13(b)) and the electron micrograph (fig. 16(b)).

The determination of small amounts of zirconium in solid solution by electron-probe analysis is difficult and gives at best poor results. In the form of an oxide, however, it will give off a visible emission when bombarded by an electron beam. Thus its presence can be qualitatively detected by visual observation. A line scan of the sample by the electron beam in the probe revealed such emission to be present. The zirconium content, however, was apparently too low to determine its variation from point to point in the specimen.

Tungsten plus oxides and tantalum. - The addition of 20 weight percent tantalum to prealloyed tungsten powders containing 5 volume percent of either hafnia or zirconia (figs. 17(a) and (b)) yielded structures that were similar in appearance to those observed with the same tungsten-base powders without tantalum shown in figures 10(b) and (c) (p. 27). The hafnia-containing composite consists of a sound, relatively clean tungsten-tantalum alloy matrix and a number of elongated dispersoids. With zirconia, the alloy matrix appeared to contain numerous voids and fissures, and the dispersoids were con-



(a) Tungsten-hafnia-tantalum (billet 26). Extrusion temperature, 4300° F.



(b) Tungsten-zirconia-tantalum (billet 29). Extrusion temperature, 4000° F.

Figure 18. - Structures of as-extruded composites based on tungsten - 5 volume percent oxide with 20 weight percent addition of tantalum. Reduction ratio, 12:1 longitudinal sections; etchant, 30 percent lactic acid, 15 percent nitric acid, 5 percent hydrofluoric acid. X18 000.

siderably larger in diameter. In addition, these elongated dispersoids contain evidence of a globular constituent.

Examination of these two materials by electron microscopy at X10 000 to X30 000 seemed to indicate that the matrix contained a smaller amount of porosity than those that did not contain the tantalum. In addition a number of fine dispersoids were distributed between the elongated particles visible in the light micrographs. With hafnia, the range of sizes of these particles was generally 0.02 to 0.5 micron with a few as large as 1.0 micron (fig. 18(a)). The zirconia-containing composite exhibited dispersoids in the range of 0.05 to 1.0 micron, with the greatest number occurring between 0.1 to 0.5 micron in diameter (fig. 18(b)).

DISCUSSION

Tungsten-base composites possessing improved high-temperature strength properties have been prepared by powder metallurgy techniques. Most of the materials studied exhibited 3000° F stress-rupture strengths that exceeded those of unalloyed tungsten, which was used as a standard. Good stress-rupture properties were obtained with composites containing either hafnia (5 volume percent) or a combination of zirconium and tantalum (0.42 to 0.47 and 5 to 15 percent by weight, respectively). The 100-hour stress-rupture strengths at 3000° F for some of the best tungsten-base materials for which data are available are plotted in figure 19. The tungsten-hafnia and tungsten-zirconium-tantalum

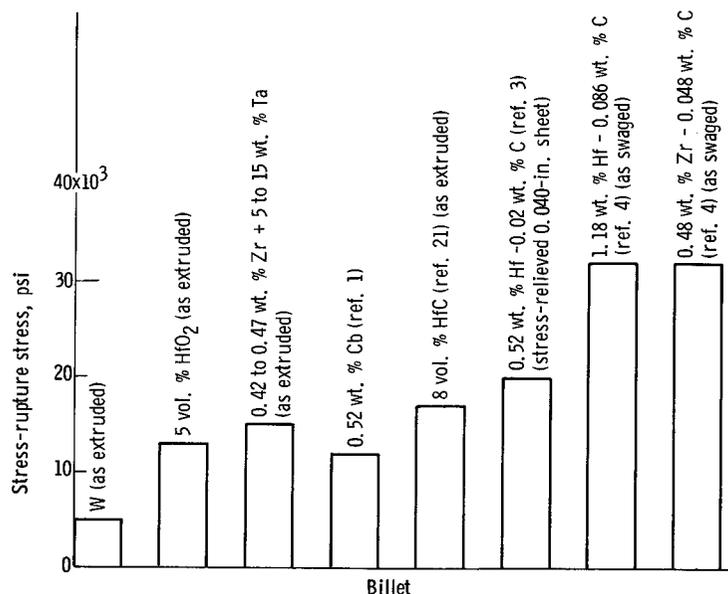


Figure 19. - Stress for 100-hour stress-rupture life of tungsten and tungsten-base composites. Test temperature, 3000° F.

composites compare favorably with these high-strength materials. Stress-rupture tests carried out at 3500^o F, although somewhat limited in number as a result of the small number of specimens available, demonstrate that some of the materials maintain a strength advantage relative to tungsten even at this temperature.

This investigation was of a preliminary nature; thus, no attempt was made to optimize either composition or processing variables. Furthermore, the observed strengthening was attained despite the fact that in most cases a uniform distribution of fine dispersoids was not achieved. Actually, in most instances, metallographic examination revealed large elongated dispersoids. Electron microscopy at considerably higher magnifications, however, did reveal the presence of some fine particles in all the materials produced.

Tungsten Plus Oxides

Of the three types of tungsten-plus-oxide composites studied, tungsten-hafnia yielded the highest 3000^o F stress-rupture strengths, which, as noted, compared favorably with the best tungsten-base materials produced to date (fig. 19). Even at 3500^o F, one of the tungsten-hafnia composites exhibited a rupture life at a stress of 8000 psi that was more than a factor of 10 greater than unalloyed tungsten. The structure of this composite contained a number of elongated oxide particles, many of which were large enough to see even at low magnifications; a few, however, were present as very fine dispersoids. In view of the nature of the dispersoid size and distribution as shown in figure 11(a) (p. 29), the high strength cannot be reasonably attributed solely to the dispersoids; thus other mechanisms may have contributed to the observed strengthening. Certainly, the presence of significantly elongated particles could lead to a strengthening effect analogous to fiber reinforcement. A strengthening increment could also have resulted from a solid solution alloying of hafnium. Inconsistencies in the chemical analyses, however, do not permit the evaluation of such an effect. Conceivably, hafnium in solid solution could act as a scavenger of interstitial impurities, which by forming a second phase would also improve the strength.

The zirconia-containing materials were generally well below tungsten-hafnia in long-time stress-rupture strengths at both 3000^o and 3500^o F. Surprisingly, however, in a shorttime tensile test at 3000^o F one of the composites containing zirconia was about 30 percent stronger than any of those containing hafnia. At 3500^o F these two composites exhibited approximately the same tensile strengths (figs. 4 and 5). In general, the microstructure of both tungsten-plus-oxide composites appeared quite similar. The tungsten-plus-zirconia composite, however, contained a greater number of the smaller dispersoids, and its larger elongated particles were generally thicker and exhibited evidence

of a globular constituent (fig. 17(b)). Thus, while microstructure gives no clue to the reason for the improved tensile strength, the difference in shape of the elongated particles may have contributed to the lower stress-rupture strengths.

The third tungsten-plus-oxide composite, tungsten-thoria, exhibited strength properties that were well below those of unalloyed tungsten. Examination of the parameters associated with this material revealed that the thoria addition resulted in a lower percent of theoretical density than either hafnia or zirconia. Presumably this lower density is associated with the greater amount of microporosity noted previously in the electron micrographic examination (fig. 11(c)). The thoriated material also had a lower hardness and a slightly finer grain size; however, these two factors probably counteracted one another. Despite further evaluation of the three oxide-containing materials, including X-ray and chemical analyses, no apparent reason other than porosity could be found to account for the low strength.

Tungsten Plus Zirconium

The presence of agglomerated and fibered oxides in almost all of the extruded products has been previously noted. One obvious exception was the tungsten-zirconium produced from the originally arc-melted material (fig. 13(a)). Although no large, fibered dispersoids were observed, the particles were quite large (0.1 to 1.5 μ) and generally segregated in grain boundary areas (fig. 15). At 3000^o F the strength was essentially the same as that realized for the composites prepared from the coprecipitated and reduced powder of the same nominal composition (fig. 14(a)); its ductility, however, was as much as an order of magnitude lower. At 3500^o F, the measured rupture life for this material at a stress of 8000 pounds per square inch was 5.5 hours. This stress-rupture life exceeds that of any of the other composites produced in this study (fig. 9). In order to gain a clearer insight into the reasons for the large difference in ductility between composites prepared from powder either produced by coprecipitation and reduction or derived from arc-melted material, as well as to determine the factors contributing to the superior high-temperature rupture properties of the latter, the measured properties of these two materials were evaluated. The composite made from the originally arc-melted material was slightly lower in percent theoretical density, but it possessed a higher hardness and a finer grain size. These last two factors are generally indicative of a higher strength and a lower ductility. In addition, this material contained a greater amount of carbon, which would also be expected to produce the same effect.

The differences in dispersoid size and distribution between the two materials was also felt to warrant consideration. The originally arc-melted material was consolidated by hot pressing in a graphite die. That such an operation could influence the dispersoid

particle morphology can reasonably be postulated. If agglomeration during densification is assumed to occur by a vapor-phase transfer of volatile suboxides, then a consolidation process such as hot pressing should be more effective in limiting dispersoid growth than the more conventional cold pressing and high-temperature sintering. Densification occurs at a lower temperature in hot pressing, thus closing much of the interconnected porosity at temperatures below those where a vapor-phase transfer mechanism could be operative. In this case, agglomeration would have to take place by the much slower processes of grain boundary and volume diffusion.

Tungsten Plus Zirconium and Tantalum

The addition of 5 to 15 percent by weight of tantalum to tungsten - 0.5 weight percent zirconium prepared by coprecipitation and reduction of mixed oxides exhibited 3000^o F strength properties that were superior to those of any of the other materials produced in this study. At 3000^o F, the 100-hour stress-rupture strength of these materials were up to three times that of unalloyed tungsten and almost twice as great as the same tungsten-zirconium without tantalum. The rupture lives of these composites at 3500^o F and 8000 psi ranged from 1.2 to 3.8 hours (table V). Although these values are below those of either tungsten-hafnia or the hot-pressed tungsten-zirconium, they are still much better than unalloyed tungsten.

The structure of this entire series of composites (figs. 14(b) and (d)) consisted of a completely alloyed tungsten-tantalum matrix with agglomerated and elongated oxides and a few small dispersed particles. The completeness of the tungsten-tantalum alloying was verified by X-ray (lattice parameter) and electron-probe analyses. In view of the nature of the oxide phase present, most of the strength improvement obtained must be associated with the alloying effect of tantalum. Surprisingly, however, variations in tantalum content between 5 and 15 percent by weight did not produce a noticeable variation in the strength level achieved. No apparent explanation for this behavior could be determined.

Two-Phase Tungsten-Zirconium-Tantalum Alloy

One of the objectives of this study was to produce a distinct two-phase (ductile and brittle) type of structure. A composite based on the originally arc-melted tungsten-zirconium powder in combination with 5 weight percent of tantalum yielded such a material. In order to accomplish this the consolidation procedure had to be modified. All the previously-described tungsten-zirconium-tantalum composites yielded structures indicative of complete solid solution alloying of the tantalum. Thus a high-pressure, low-

temperature hot-pressing operation was substituted for either high-temperature, low-pressure hot pressing or conventional cold pressing and high-temperature sintering. The results indicated that this technique did yield the desired structure. In addition, however, fine dispersions of particles were observed throughout the matrix (fig. 16(a)).

Because of machining difficulties, only two specimens of this two-phase material were available for testing. At 3000^o F and 8000 psi the stress-rupture life was 379 hours, while at the same temperature and 7000 psi it was greater than 881 hours. The strength of this material appears to be due to the combination of the two-phase structure and the uniform distribution of dispersoids. A significant additional benefit derived from this type of composite was the ease of extrusion. Table IV shows that the originally arc-melted and comminuted tungsten - 0.5 weight percent zirconium material extruded at 12:1 and 4200^o F required a maximum extrusion pressure of 197 000 psi for a ram speed of 6.6 inches per second. The same tungsten-zirconium with 5 weight percent tantalum extruded at 12:1 and 4000^o F required a maximum extrusion pressure of only 115 000 psi for a ram speed of 8.0 inches per second. This would seem to indicate that the presence of the tantalum-rich phase resulted in improved plasticity during extrusion.

Tungsten Plus Oxides and Tantalum

The tungsten-plus-oxides-and-tantalum composites all contained 20 weight percent tantalum. Extrusion of these materials was quite difficult under the conditions employed, and only the one based on tungsten-hafnia yielded any material suitable for testing.

Conceivably a lower tantalum addition would have yielded more desirable results.

SUMMARY OF RESULTS

An exploratory investigation conducted to determine the high-temperature strength properties of as-extruded tungsten-base composites or dispersion-strengthened tungsten produced by novel powder metallurgy techniques yielded the following results:

1. Most of the materials studied exhibited 3000^o F stress-rupture strengths that greatly exceeded those of unalloyed tungsten. Although somewhat limited in scope, rupture tests at 3500^o F also indicated an appreciable strength advantage relative to tungsten. This strengthening occurred despite the fact that a uniform distribution of fine dispersoids was generally not achieved.

2. At 3000^o F, the 100-hour stress-rupture strength of a tungsten - 5 volume percent hafnia composite was approximately twice that of unalloyed tungsten. At the same temperature and 8000 pounds per square inch, the extrapolated rupture life was more than

three orders of magnitude greater than that of unalloyed tungsten. This relative improvement in rupture life was still a factor of 10 at 3500^o F. These properties are comparable to some of the best tungsten alloys and composites presently available. Strengthening observed with this material is believed to result from a combination of fine dispersoids, fiber reinforcement, and solid solution alloying of hafnium.

3. Composites consisting of tantalum additions (5 to 15 percent by weight) to tungsten - 0.5 weight percent zirconium prepared by coprecipitation and reduction exhibited 100-hour stress-rupture strengths at 3000^o F that were the highest obtained in this study (three times that of unalloyed tungsten). The strength of these composites is attributed mostly to the alloying effect of tantalum. Variations in tantalum content between 5 and 15 percent by weight did not, however, produce a noticeable variation in the strength level achieved.

4. Tungsten - zirconia exhibited 3000^o F tensile strengths that were as much as 30 percent greater than those of the best tungsten-hafnia material. The stress-rupture strengths of specimens from this composite were, however, considerably below those of tungsten - hafnia. An unidentified globular constituent in the elongated zirconia particles may account for the low rupture strengths.

5. Tungsten - thoria composites exhibited stress-rupture strengths that were well below those of even unalloyed tungsten. Low density resulting from microporosity is believed responsible for the poor strength.

6. Tungsten-zirconium composites prepared from powders produced either by coprecipitation and reduction of oxides or by arc-melting and comminution exhibited similar 3000^o F strength properties. In contrast, the ductility of the two materials was quite different; that is, the uncleaned coprecipitated and reduced materials were more ductile than unalloyed tungsten, whereas both the same material with hydrogen precleaning and the originally arc-melted material were very brittle.

7. A two-phase (one tungsten-rich and one tantalum-rich) tungsten - 0.47 weight percent zirconium plus 5 weight percent tantalum composite was produced by using a low-temperature, high-pressure hot-pressing technique. The strength of this composite, while slightly below that of the other tungsten-zirconium-tantalum materials, was almost twice that of unalloyed tungsten and is believed to be due to the combination of the two-phase structure and the uniform distribution of fine particles throughout the entire matrix. An additional benefit derived from the two-phase structure was the ease of extrusion, presumably associated with improved plasticity resulting from the presence of the tantalum-rich phase.

8. Composites containing 20 weight percent tantalum generally did not yield successful extrusions.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, April 25, 1966,
129-03-01-05-22.

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